

Fluorine-Assisted Stabilization of Cubic Phase Boron Nitride Polycrystalline Solids

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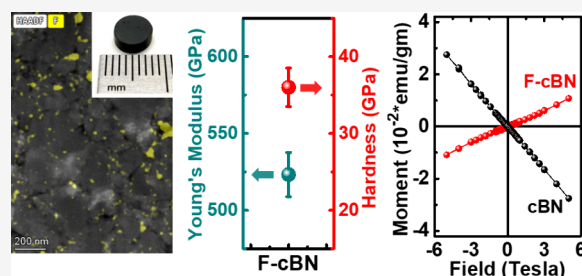
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ABSTRACT: The synthesis of cubic boron nitride (cBN) solids by consolidation of cBN powders at high pressure and high temperature (HPHT) is challenging, as it leads to the hexagonal BN (hBN) phase. Here we report an HPHT synthesis of polycrystalline fluorinated cBN (F-cBN) solids that show twinned nanodomains, the presence of F at the grain boundaries, and excellent mechanical hardness and second-order nonlinear susceptibility. In contrast to pure diamagnetic cBN, we found that F-cBN is paramagnetic at room temperature, as confirmed by electron paramagnetic resonance spectroscopy, suggesting the role of defects in tuning the magnetic properties of cBN. Density functional theory calculations reveal that F stabilizes the cBN phase by passivating the dangling bonds and, in addition, forms substitutional defects (F_N) leading to F_N-V_B defect complexes that generate local magnetic moments. These properties of F-cBN might lead to new applications of cBN and also open a pathway to synthesize new metastable phase materials with emergent properties.

KEYWORDS: cubic BN, fluorination, nanodomains, properties, density functional theory



Cubic boron nitride (cBN), the second hardest known material after diamond,¹ has attracted ample interest as an ultrawide-bandgap (UWBG) diamagnetic semiconductor due to its exceptional mechanical,² thermal,³ and chemical stability.⁴ It is widely regarded as superior to diamond for many practical applications because of its excellent chemical and thermal stability under extreme conditions.⁵ Unlike diamond, which oxidizes and forms graphite at high pressure and high temperature (HPHT),⁶ cBN is chemically inert and exhibits superior oxidation resistance,⁴ enabling reliable performance in high-speed machining and cutting tool industries.⁷ However, applications of pure phase and doped cBN remain limited^{8–10} due to the lack of its synthesis in crystalline form,¹¹ owing to its metastable nature.¹²

Synthesis and phase stability¹³ of crystalline cBN solids using its own precursor remains challenging, as at HPHT, metastable cBN transforms to the hexagonal BN (hBN) phase,^{4,14–16} the most stable polymorph of BN at ambient conditions.¹⁷ Typically, cBN microcrystals are produced by using other BN phases as a starting material,^{2,18–23} and in the presence of catalysts or solvent^{24–28} that helps in reducing the energy barrier for the hBN-to-cBN phase transformation and facilitates the nucleation process. Regarding the use of catalysts or solvents, introducing fluorine (F) during the BN film

synthesis is shown to preferentially etch hBN,^{29–32} promoting the cBN phase formation.^{33–35} Interestingly, during this fluorination process, being a highly electronegative element, F can modify the bonding arrangements and local electronic structure, hence induce new properties.^{8,9,36,37}

Here, we stabilized cBN phase solids at HPHT by using fluorinated cBN precursor powders, in which F acts as a passivation layer and prevents the hBN phase transformation. The polycrystalline fluorinated cBN (F-cBN) solid exhibits excellent mechanical properties and nonlinear optical second-harmonic generation. It also shows paramagnetic behavior, in contrast to diamagnetic cBN, as supported by density functional theory (DFT) calculations, suggesting how the fluorination not only stabilizes the cBN phase but also generates defect complexes that induce local magnetic moments. Synthesis of F-cBN solids would be useful for

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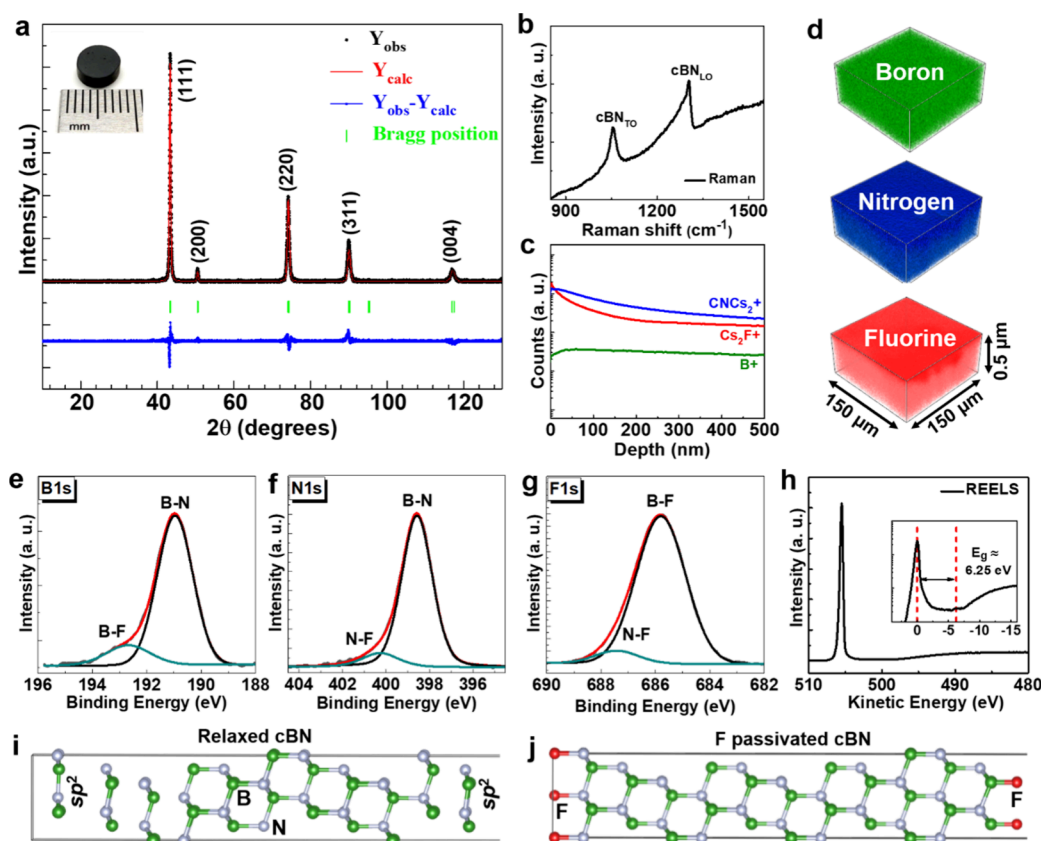


Figure 1. Characterizations of the F-cBN solid. (a) X-ray diffraction of F-cBN polycrystal showing respective oriented Bragg peaks of cBN. From Rietveld analysis the obtained cubic lattice parameters are ~ 3.61395 Å. The inset shows an HPHT sintered F-cBN crystal. (b) Raman spectroscopy shows transverse optical (TO) and longitudinal optical (LO) phonon modes, characteristics of cBN. (c, d) TOF-SIMS depth profile shows that F is distributed throughout the bulk, along with B and N. (e–g) Core-level XPS scan shows the presence of majority B–F bonds with minority N–F bonds. (h) From reflection electron energy loss spectroscopy, we obtained a bandgap of ~ 6.25 eV. (i) Transformation of a nonpassivated (111) cBN slab to an sp^2 hBN ground state structure during relaxation. (j) Passivation with F on both sides of the (111) cBN surface prevents the sp^2 graphitization process. In the structures, atoms are B (green), N (gray), and F (red), respectively.

demanding condition optoelectronics, along with its machining and cutting tool applications.^{7,38,39}

We synthesized fluorinated cubic BN (F-cBN) solids by using HPHT sintering at 1550–1600 °C temperature and 6.5–7.0 GPa pressure (see Methods in the Supporting Information). As a starting material, we used cBN nanopowders which were fluorinated using the gas phase fluorination process to produce F-cBN powders (Supporting Information Figures S1 and S2). After HPHT sintering of F-cBN powders, we obtained black color solids (inset, Figure 1a). We performed X-ray diffraction (XRD) of the F-cBN solid that shows all the cBN Bragg peaks (Figure 1a), and no diffraction peaks corresponding to hBN are observed, indicating it is a pure phase polycrystal (whereas HPHT sintered pure cBN powders produce a mixed hBN+cBN phase solid, Figure S3). From Rietveld analysis, we obtained cubic lattice parameters as $a_c = 3.61395$ Å, with $a \sim 0.05\%$ lattice compression with respect to pure cBN (3.6160 Å).⁴⁰ Raman spectroscopy shows transverse optical (TO ~ 1054.1 cm^{-1}) and longitudinal optical (LO ~ 1304.5 cm^{-1}) phonon modes, characteristics of cBN (Figure 1b).¹³ The asymmetrically broadened phonon modes indicate the presence of defects in the cBN lattice.¹³ To confirm the presence of F, we performed a time-of-flight secondary-ion mass spectroscopy (TOF-SIMS) depth profile and corresponding elemental maps that showed the presence of B, N, and F, down to a measured depth of 0.5 μm (Figures 1c and 1d). X-

ray photoelectron spectroscopy (XPS) further confirms the presence of F with ~ 7.7 at. %, and they are mostly bonded with B, forming mostly B–F bonds (~ 685.8 eV) with a minor number of N–F bonds (~ 687.43 eV) (Figures 1e–g).⁴¹ Since F is electronegative, it is expected that the F atoms preferentially bond to B atoms, forming B–F bonds. Further, the measured density (using the solid cylindrical method) and bandgap (from reflection electron energy loss spectra, REELS) of the F-cBN solid are ~ 3.3 g/ cm^3 and ~ 6.25 eV, respectively (inset in Figure 1h).¹³

We provide the cBN phase stability mechanism via F incorporation by performing DFT calculations. First, we studied the stability of pure cBN (111) (most energetically stable facet) slabs without surface functionalization. When such slabs are relaxed, they gradually transform into the sp^2 -bonded hBN phase (Figures 1i, S4a, and S4b). This process of transformation begins from the surface and then advances to the central regions of the slab, until the entire structure becomes sp^2 -bonded. The “graphitization” process is precipitated by the presence of dangling bonds on the surface and the subsequent contraction of the existing bonds between the atoms on the surfaces. The latter process reduces the surface energy, but results in the development of the sp^2 -character, which induces the cBN-to-hBN phase transformation.^{42,43} The surface functionalization via F changes this “graphitization” process. If we fluorinate the cBN slab on both sides, the F

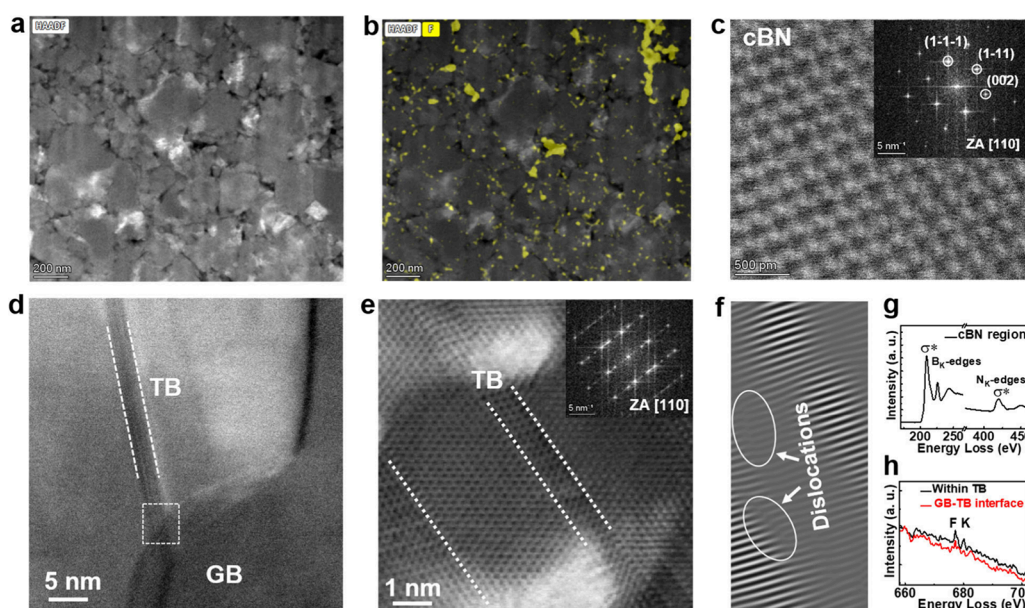


Figure 2. Microstructural characterizations of F-cBN solid. (a, b) HAADF-STEM image and its corresponding STEM EDX showing elemental mapping of fluorine predominantly at the grain boundary. (c) High-resolution ABF-STEM image shows cBN inside the bulk/grain viewed along the $[110]$ zone axis and corresponding FFT pattern (inset). (d) ADF-STEM image showing grain boundaries (GBs) along with the presence of twin boundaries (TBs). (e) ABF-STEM image of nanotwinned domains at atomic scale and its corresponding FFT pattern (inset) viewed along the zone axis $[110]$. (f) Lattice images of dislocations within TBs (marked by white rings) constructed by IFFT. (g, h) STEM EELS within the grain shows the cBN phase, and the white boxed region (of (d)) shows the presence of F in both TB and at the TB–GB interface regions.

atoms passivate the dangling bonds, lowering the surface energy and restoring the sp^3 -bonding at the cBN surface (Figures 1j, S4c, and S4d). The F adatoms also partially cancel the built-in electric field (E) inside the slab, which exists due to the polar nature of the (111) surface.^{44,45} This effect is long-ranged, making the nonpassivated surface susceptible to the influence of F adatoms from the opposite surface.

Since F is electronegative, it is expected that the F atoms would preferentially bond to B atoms on the surface, forming strong B–F bonds. But the question arises whether F will also bond with N atoms on the surface, such as when the slab is fluorinated on both sides, and if the cubic phase is stable in this case. Our calculations show that such a slab is indeed stable and not subject to graphitization. To compare the stabilization effect of F on the N- and B-terminated surfaces, we calculated the corresponding surface formation energies defined as

$$E_{\text{surf}} = E_{\text{two-sided F}} - E_{\text{one-sided F}} - n\mu_{\text{F}} \quad (1)$$

where $E_{\text{two-sided F}}$ is the total energy of the system with F atoms on both sides, $E_{\text{one-sided F}}$ is the energy of the same system but without F atoms on the surface (B- or N-terminated), n is number of the F atoms removed from the surface, and μ_{F} is the fluorine's chemical potential. The latter is obtained by halving the total energy of the F_2 molecule. In our calculations, μ_{F} was found to be -1.800 eV. The calculations give $E_{\text{surf}} = -1.411$ eV (per F atom) for the N-terminated surface and $E_{\text{surf}} = -5.269$ eV for the B-terminated one. Thus, although F stabilizes both the surfaces, the B-terminated surface is stabilized to a greater extent. These indicate that the cBN phase can be stabilized against its transformation to the sp^2 -bonded structure via F, with the formation of a high-degree of B–F regions.

We investigated the microstructure of the F-cBN material by using cross-sectional high-resolution scanning transmission electron microscopy (HR-STEM) by preparing a focused ion beam (FIB) lamella. The high-angle annular dark-field

(HAADF)-STEM image shows the randomly oriented grains with sizes of ~ 100 – 400 nm (Figure 2a). The STEM EDX map shows the presence of F at a higher percentage near the grain boundaries (GB) (Figure 2b), compared to the bulk. The high-magnification annular bright field (ABF)-STEM image and its corresponding fast Fourier transform (FFT) reveal the cubic phase within the grain (Figure 2c). The interplanar $d_{(111)}$ spacing is around 2.1 Å. We also observed frequent formation of nanotwinned domains with sizes of a few nm, shown in the low-magnification annular bright field (ADF) and high-resolution ABF-STEM images (Figures 2d and 2e).^{2,46,47} A region with twin boundary (TB) domains (Figure 2e) is analyzed by inverse fast Fourier transform (IFFT) to identify dislocations (Figures 2f and S5).^{46,48} Electron energy loss spectroscopy (EELS) confirms the cBN (within the grain) and the presence of F both within the TB and at the TB–GB interface (Figures 2g and 2h).

During the HPHT sintering process, F atoms may also get incorporated within the lattice, particularly in the vicinity of TBs. However, its direct imaging using ADF and ABF-STEM remains challenging as F, a light element, is difficult to distinguish from B and N at the atomic scale due to comparable atomic number and thickness-dependent contrast variations in the sample. Such incorporation of F at the vicinity of TB may lead to the creation of substitutional defects/vacancies. We provide theoretical insights about the possible location of F by considering three positions of it in the cBN matrix within the slab: (1) closer to the substrate, (2) in the middle of the slab, or (3) closer to the F-passivated B-surface. We use N–H bonds as a stand-in for the substrate. These calculations were performed for a $4 \times 2 \times 2$ slab supercell. Since our bulk defect formation energy calculations show that out of different possible fluorine defects, nitrogen-substituted fluorine (F_{N}) is lowest in energy (Figure S6), we placed F_{N} in the aforementioned positions (Figure S7). Taking the defect

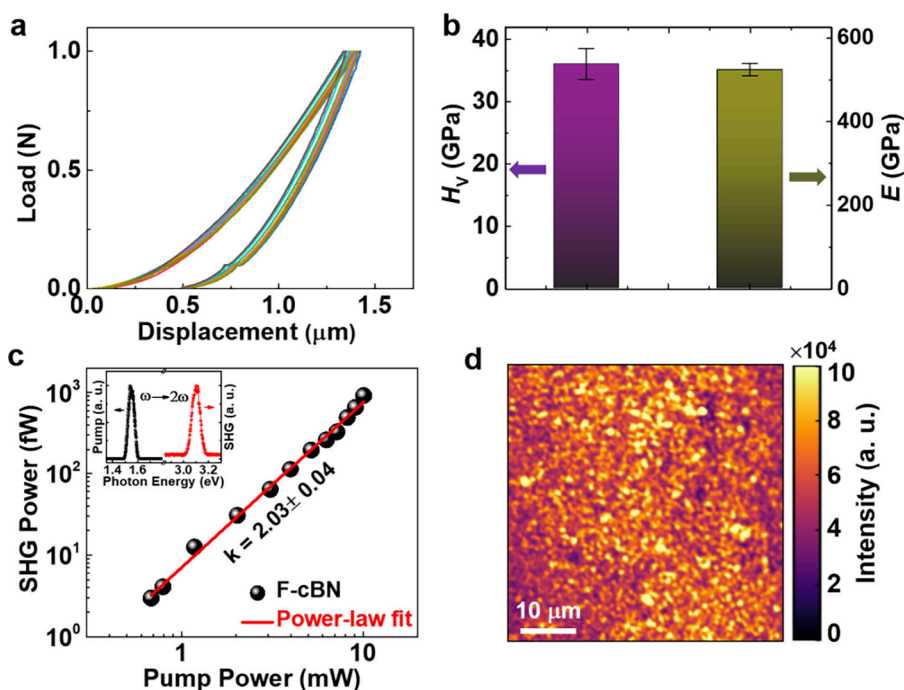


Figure 3. Mechanical and nonlinear optical behavior of the F-cBN solid. (a) The load–displacement curves obtained during the nanoindentation process at several points (represented by different colors) of the solid surface. (b) The measured Vickers hardness (H_V) and Young's modulus (E) of the solid. (c) SHG intensity from the solid surface as a function of pump power, exhibiting a quadratic dependence. SHG spectrum confirming frequency doubling of the 800 nm excitation (inset). (d) SHG intensity map of the F-cBN surface, where spatial variation originates from polycrystalline domains.

formation energy closest to the N–F surface as reference, the corresponding energies are 0 eV for F_N near the N–F surface, -1.39 eV away from the two surfaces, and -4.21 eV closest to the B–F surface. Hence, the defect forms most readily when F_N is closest to the B–F surface and F_N atoms will cluster closer to the B–F surface.

Formation of twinned domains during cBN synthesis is interesting, as it amplifies various properties.^{2,46,49,50} Regarding the formation of nanotwinned domains (Figure 2e), we calculated the TB energy, γ_{TB} , by using the following expression:⁵¹

$$\gamma_{TB} = \frac{E_{TB} - N_{TB}E_{Bulk}}{2A_{TB}} \quad (2)$$

where E_{TB} is the energy of the supercell with two TBs, N_{TB} is the number of atoms in this supercell, E_{Bulk} is the energy per atom in an ideal BN crystal, and A_{TB} is the surface area for each of the two TBs. The energies E_{Bulk} were found for the ideal $1 \times 1 \times n_3$ supercells (with $n_3 = 2$ or 3), from which the structures with TBs are then created. Both ideal structures give the same E_{Bulk} per atom (Supporting Information Table S1). Using $A_{TB} = 11.3702 \text{ \AA}^2$ in eq 2, along with the data (Table S1), we find that the cost of creating a TB is $\gamma_{TB} = 4.965 \text{ meV/\AA}^2$ or 79.54 mJ/m^2 , agreeing well with a literature report (81.72 mJ/m^2).⁵⁰ It should be pointed out that γ_{TB} in cBN is, in fact, extremely low, with the typical values for γ_{TB} ranging from 300 to 1000 mJ/m^2 in other materials.^{52,53} It is important to note, however, that if we want to obtain a TB by shifting one-half of an ideal cBN crystal relative to the other, the energy barrier for such a shift would be very large. The minimum surface energy of the stacking fault corresponding to the barrier is approximately 4000 mJ/m^2 , ~ 50 times greater than γ_{TB} .⁵⁰ The low energy of TB formation implies that such boundaries might be generated

in large numbers during the growth (rather than shear deformation).

Considering the mechanical robustness of cBN, we evaluated the mechanical properties of the F-cBN solid using both nanoindentation and Vickers hardness testing. Measurements were performed at multiple locations to assess the homogeneity. The nanoindentation load–displacement curves are consistent across the tested regions (Figure 3a), yielding a Young's modulus (E) of $523 \pm 14 \text{ GPa}$. The measured Vickers hardness (H_V) of the F-cBN solid is $36 \pm 2.5 \text{ GPa}$ (Figure 3b). Representative Vickers indentation imprints are also shown (Figure S8). The obtained hardness value is slightly lower than the nanotwinned cBN crystals,^{2,54–56} as the mechanical properties depend on the microstructure and crystallinity.^{11,23,46}

We probed the nonlinear optical response of the F-cBN solid using reflection-geometry second-harmonic generation (SHG). Cubic BN crystallizes in the noncentrosymmetric zinc-blende structure (space group $F\bar{4}3m$), enabling electric-dipole-allowed SHG.^{36,57–59} Fluorination preserves the cubic phase and its intrinsic noncentrosymmetry. Under 800 nm ($\sim 1.55 \text{ eV}$) femtosecond excitation, a clear SHG signal is observed at 400 nm ($\sim 3.10 \text{ eV}$) (inset of Figure 3c). The SHG intensity follows a near-quadratic power dependence, $I_{SHG} = AP_{pump}^k$, with $k = 2.03 \pm 0.04$, confirming a second-order nonlinear optical process (Figure 3c). No evidence of sample degradation or higher-order nonlinear emission was observed within the explored excitation range. Spatially resolved SHG mapping reveals strong intensity variations across μm -length scales (Figures 3d and S9a), reflecting the polycrystalline microstructure of F-cBN. The observed spatial variation arises from the superposition of SHG contributions from multiple randomly oriented domains within the optical excitation

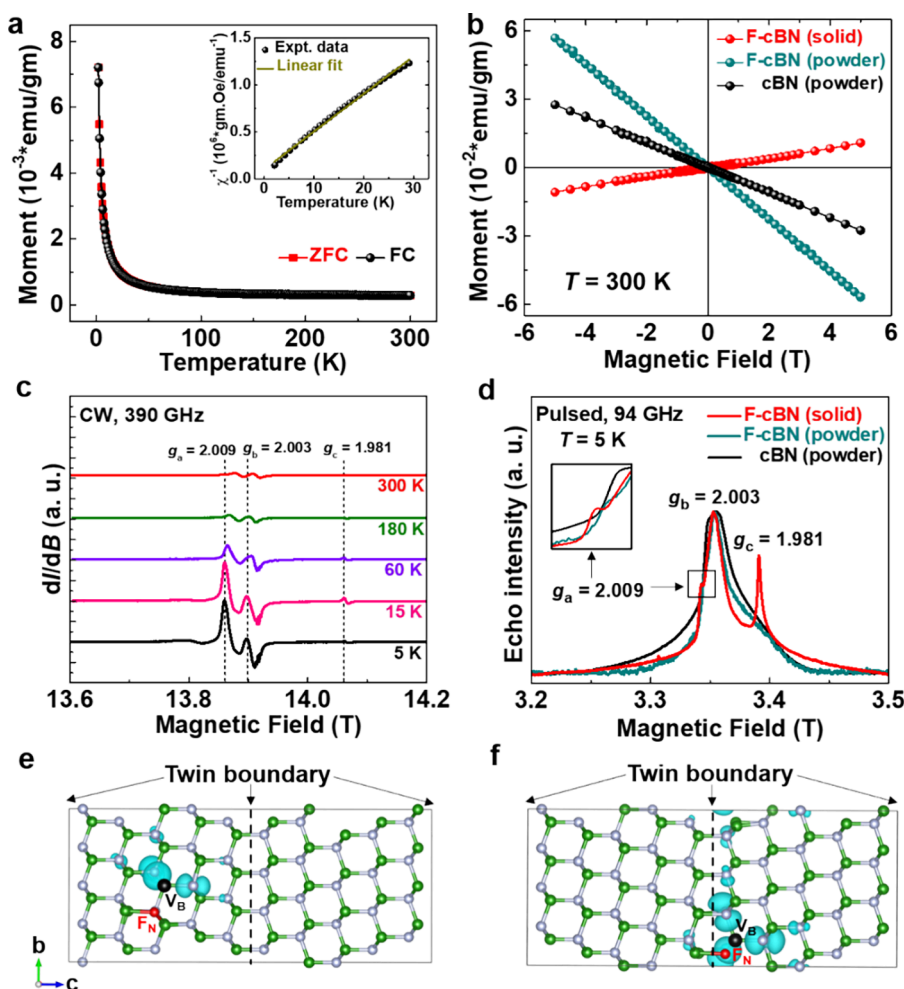


Figure 4. Paramagnetism in the F-cBN solid and its theoretical insights. (a) Temperature-dependent magnetization (M) of the F-cBN solid. Linear T -dependence of the inverse susceptibility (χ^{-1} vs T) indicates the paramagnetic behavior (inset). (b) Magnetic field (H)-dependent magnetization also shows paramagnetic behavior. For comparison, diamagnetic behavior is observed for cBN and F-cBN powders. (c, d) Temperature-dependent continuous wave (CW) high-field EPR and echo-detected (pulsed) field sweep EPR show an additional peak with a $g_c \sim 1.981$, compared to cBN and F-cBN powders. For clarity the zoomed-in region of the g_a peak is shown (inset, boxed). (e, f) Theoretical calculation of the spin-defects producing net magnetic moments. The $4 \times 2 \times (4-2/3)$ supercell with a substitutional defect-boron vacancy (F_N-V_B) complex in two different positions: (e) between TBs and (f) at the TB. The spin density isosurfaces associated with the defects are shown (cyan color). In both cases, the F_N-V_B defects possess high spin states, creating local magnetic moments. Atoms are B (green), N (gray), F_N (red), and V_B (black), respectively.

volume. Notably, the SHG response of the F-cBN solid is comparable in magnitude to that of cBN nanopowders (Figures S9b and S9c), previously observed for much larger grain sizes.⁶¹ Importantly, fluorination does not alter the intrinsic noncentrosymmetry of cBN, which allows electric-dipole SHG.

Another interesting property found from magnetic investigation is that F can induce or modify local magnetic behavior in cBN, which is otherwise a diamagnet in its pristine form. We measured magnetization of the F-cBN solid (both in zero field cooled (ZFC) and field cooled (FC)), which shows paramagnetic behavior (without any detectable magnetic ordering) down to 2 K (Figure 4a). The inverse susceptibility (χ^{-1}) exhibits a linear relationship (inset, Figure 4a), consistent with the Curie law, indicating the paramagnetic behavior, as observed for fluorinated graphene.⁶² The M - H loop at room temperature clearly indicates paramagnetic behavior (Figure 4b). To exclude the possibility of extrinsic magnetic impurities, the elemental composition was analyzed using the energy-dispersive X-ray fluorescence (EDXRF) technique. EDXRF

analysis did not show any considerable traces of magnetic impurity elements (Tables S2 and S3), indicating the intrinsic origin of the observed paramagnetic behavior in the polycrystal. For comparison, we also measured the M - H loop for pure cBN and F-cBN nanopowders, showing diamagnetism, as neither B nor N has unpaired electrons.

To confirm paramagnetic behavior, we also performed electron paramagnetic resonance (EPR) spectroscopy. The X-band and low-frequency continuous wave (CW) EPR spectra did not allow the g anisotropy to be fully resolved (Figures S10 and S11).⁶³ The temperature-dependent high-field CW EPR (Figure 4c) and echo-detected pulsed EPR measurements (Figure 4d) detected three distinct g -values, labeled as $g_a = 2.009$, $g_b = 2.003$, and $g_c = 1.981$, confirming intrinsic paramagnetic behavior of the F-cBN solid.^{64,65} The higher g -values are close to free electrons of BN.⁶⁵ The additional intense $g_c = 1.981$ peak for the F-cBN solid (as compared to the powder) appears possibly due to weakly coupled spin-1/2 defect states, i.e., spins that are near enough to have some coupling between them. To quantitatively correlate the

magnetization with the EPR-active defect centers, we estimated the spin concentration from the susceptibility using Curie-law analysis for an isolated spin $S = \frac{1}{2}$ paramagnetic system. From the magnetic susceptibility, we extracted the mass Curie constant as $C_g = 2.67 \times 10^{-5}$ emu·K/g·Oe. The spin concentration was then calculated using the Curie expression as

$$C_g = \frac{Ng^2\mu_B^2S(S+1)}{3k_B} \quad (3)$$

where N is the number of spins per gram, k_B is the Boltzmann constant, μ_B is the Bohr magneton, and $S = \frac{1}{2}$. The g -value was $g_{\text{avg}} = 1.998$, obtained from the principal values determined by high-field EPR ($g_a = 2.009$, $g_b = 2.003$, and $g_c = 1.981$). This yielded a spin concentration of $N = 4.23 \times 10^{18}$ spins/g. This is in close agreement with the reported value for defect-rich BN determined by quantitative EPR.⁶⁶ This indicates that the observed paramagnetic behavior originates from intrinsic fluorination-induced defect centers.

About the origin of paramagnetism, we considered the possibility of forming complexes of a well-known spin defect in cBN, e.g., V_B ,^{67,68} and F_N . In bulk, V_B has a formation energy of -4.48 eV in the presence of F_N (at the nearest neighboring site), which is much lower than its formation energy (5.12 eV), in the absence of F. Hence, V_B would form more readily in the presence of F_N within the bulk. This could be attributed to an attractive electrostatic interaction between V_B (a p -type defect) and F_N (an n -type defect).¹⁰ In order to see if the formation energy of V_B is also lowered when F passivates the dangling bonds on the surface, we calculated the formation of V_B in the F-terminated cBN slab (Figure S12). Calculations indicate that even if F remains on the surface, the formation energy of V_B is reduced by 0.9 eV as compared to its formation energy in F-free cBN. We also investigated the interaction of F_N and F_N - V_B with TBs. We used two equilibrium geometries: (1) an F_N defect placed between the two TBs and (2) the F_N at the TB itself (Figure S13). We found that the first structure is 496.0 meV lower in energy compared to the second one, which indicates that F_N by itself will preferentially form away from TBs. In contrast to F_N defects, the F_N - V_B defect complexes prefer to be located near the TBs rather than away from them (Figures 4e and 4f). The structure with F_N - V_B defect complexes near the TBs is lower in energy than F_N - V_B defect complexes away from the TBs by 64.4 meV. Another important difference between the simple F_N defect and the F_N - V_B defect complexes is that, whether near or farther away from the TBs, the latter possess a magnetic moment of $1.0 \mu_B$. Most of this magnetic moment is contributed by the nearest neighboring N atoms at the V_B site, as seen from the spin-density distributions. The origin of the local magnetic moments lies in the nature of the defect states that are derived from the sp^3 -hybridized $2s$ - and $2p$ -orbitals of the N atoms surrounding the V_B . Since the $2s$ - and $2p$ -orbitals of N, O, and C, are spatially localized, there are large exchange interactions between the unpaired electrons in the dangling bonds.^{69–71} The large exchange interactions, in turn, are responsible for the spin-splitting and the development of net magnetic moment associated with the defect. The paramagnetism in the F-cBN crystal is significant because it provides valuable insight into the nature and distribution of defect-induced localized electronic states. Since defects strongly influence the functional

properties, the observed paramagnetism provides a pathway in understanding defect-induced magnetic states in UWBG cBN which could be relevant to defect engineering, spintronics, and quantum technologies, where localized spins are being explored as quantum-active centers.

In conclusion, at HPHT, by using fluorinated cBN nanopowders, we have successfully stabilized the cBN phase polycrystalline solids exhibiting twinned nanodomains and the presence of F at the grain boundaries, acting as a passivation layer that helps in stabilizing the cubic phase. Unlike conventional approaches that rely on phase transformation from other BN phases, our strategy opens a direct pathway to producing cBN solids from their own precursor. This approach could also be applied for other metastable materials that remain challenging from a synthetic point of view. Further, F-cBN exhibits excellent mechanical properties, robust second-order optical nonlinearity, and paramagnetic behavior. We provided insights into the phase stability due to fluorination (suppressing the sp^2 graphitization process) and the origin of magnetism (attributed to substitutional defects and adjacent vacancies) from DFT. Observation of unique properties in cBN will make it useful for various demanding-condition applications.

■ ASSOCIATED CONTENT

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.6c02285>.

Methods, various experimental results (XRD, EDXRF, SEM, TEM, SHG, and EPR), theoretical DFT calculations, and tables (PDF)

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Author Contributions

[#]A. B., V. N. K., and P. M. A. conceptualized the work. We would like to thank Dr. Valery N. Khabashesku (Adjunct Professor at Rice University, USA), who synthesized the F-cBN powder materials. He obtained the F-cBN polycrystalline materials from his close collaboration with Dr. Vladimir P. Filonenko at Vereshchagin Institute of High-Pressure Physics of the Russian Academy of Sciences, Troitsk, Moscow, Russia. A. B., J. M., and S. C. performed the structural characterizations. R. S., T. M., and C. K. performed the electron microscopy. T. A. M. R. S. and H. Z. performed the optical second-harmonic generation. J. H. and S. H. performed the EPR spectroscopy. I. I. N., S. K. N., and P. D. performed theoretical calculations. S. K., C. W. C., and L. D. measured magnetization. S. Y., L. L., Y. Z., and T. F. performed the nanoindentation. T. T. performed the TOF-SIMS. A. B. and P. M. A. analyzed the data. All the authors discussed the results and contributed to the manuscript preparation. I. N., R. S., T. A. M. R. S., J. H., S. K., and S. Y. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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