Tunable, Multifunctional Ceramic Composites via Intercalation of Fused Graphene Boron Nitride Nanosheets

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ABSTRACT: Ternary two-dimensional (2D) materials such as fused graphene–boron nitride (GBN) nanosheets exhibit attractive physical and tunable properties far beyond their parent structures. Although these features impart several multifunctional properties in various matrices, a fundamental understanding on the nature of the interfacial interactions of these ternary 2D materials with host matrices and the role of their individual components has been elusive. Herein, we focus on intercalated GBN/ceramic composites as a model system and perform a series of density functional theory calculations to fill this knowledge gap. Propelled by more polarity and negative Gibbs free energy, our results demonstrate that GBN is more water-soluble than graphene and hexagonal boron nitride (h-BN), making it a preferred choice for slurry preparation and resultant intercalations. Further, a chief attribute of the intercalated GBN/ceramic is the formation of covalent C−O and B−O bonds between the two structures, changing the hybridization of GBN from sp² to sp³. This change, combined with the electron release in the vicinity of the interfacial regions, leads to several nonintuitive mechanical and electrical alterations of the composite such as exhibiting higher Young's modulus, strength, and ductility as well as sharp decline in the band gap. As a limiting case, though both tobermorite ceramic and h-BN are wide band gap materials, their intercalated composite becomes a p-type semiconductor, contrary to intuition. These multifunctional features, along with our fundamental electronic descriptions of the origin of property change, provide key guidelines for synthesizing next generation of multifunctional bilayer ceramics with remarkable properties on demand.

KEYWORDS: graphene–boron nitride, ceramic composites, intercalation, electrical properties, mechanical properties

1. INTRODUCTION

In the field of composites, which includes ceramic composites, the use of graphene and hexagonal boron nitride (h-BN) has been mainly discussed in mechanical terms. Recent progresses in graphene and h-BN synthesis and the introduction of graphene oxide (GO) have paved the way for the new generation of ceramic nanocomposites.¹⁻³ Recently, a study by Shahsavari et al.¹⁻³ demonstrated the mechanical properties of intercalated h-BN/tobermorite—as a representative ceramic composites, including the compressive and tensile strengths, stiffness, strain, and toughness as well as deformation mechanisms of the aforesaid ceramic composites. Other groups have also investigated the dispersion of h-BN in cement-based alkaline environments and show that an addition of 0.003 wt % h-BN increased the tensile and compressive strength by 8 and 13%, respectively.⁵ Or another group⁶ used 0.03% wt % GO in cement to successfully enhance its mechanical properties.

A key concern in graphene-based ceramic composites is typically the inability of graphene to homogeneously disperse in the composites; that is, the agglomeration of graphene in the water and/or slurry matrix makes it impossible to fully utilize its properties in the composites.⁷⁻⁸ To address this problem, graphene is chemically oxidized to produce GO. This process reduces the mechanical and electrical properties of the graphene by transforming a proportion of the sp² hybridization to sp³.⁹ Similar procedures are performed on h-BN in order to introduce some changes to its mechanical and electrical properties.⁵,¹⁰ The functional groups attached to the graphene nanosheet (as a result of the oxidation) replace the carbon as the main sources of interactions between graphene and the surrounding matrix, thus impacting significantly the electrical properties of the composites.¹¹ In this work, we present a novel approach to predict the necessary dispersions (and thus properties) in a ceramic matrix (cement) by using a ternary hybrid of graphene and hexagonal boron nitride (GBN). This

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improved dispersion is possible via low polarity of h-BN which provides acceptable covalent bondings with the silicate chains in the matrix.

The rare electronic and mechanical properties associated with the monolayer hybrid of GBN, such as variable band gap, magnetism, and Young’s modulus have attracted much attention in this unique ternary nanosheet. GBN can be produced from a fusion of graphene and h-BN. h-BN has a hexagonal structure similar to that of graphene but with an alternating composition of boron and nitrogen, instead of carbon atoms. In the ternary hybrid GBN, although graphene offers several desirable properties such as zero-gap semiconductor applicable to many technological applications, h-BN portrays significant thermodynamic and chemical stability and strong mechanical properties while electrically insulating. Thus, the combination of the two enables tunable complementary properties. The hexagonal structural similarities between the h-BN and graphene facilitate creating such hybrid structures with tunable ratios of carbon to boron and nitrogen stoichiometry. Indeed, two-dimensional hybrid GBN is now a primary research topic because of possessing the best of the two materials including significant intrinsic strength and tunable electronic structure. For example, reinforcing GBN filler in polymer composites could give rise to exotic multifunctional properties. Similarly, the intercalation of such GBN in cements and ceramics can lead to infrastructure materials with multiple desired properties including enhanced mechanical properties and self-sensing ability.

In this context, given that concrete is the most widely used construction material, such multifunctional GBN fillers can demonstrate widespread impact in infrastructure materials. However, effective engineering of such multifunctional infrastructure materials hinges on fundamental understanding, identification of limiting mechanisms, and tracing their lineage into the atomic and subatomic properties, which are all poorly understood.

Herein, we focus on a series of GBN-ceramic composites and study their electrical and mechanical properties using density functional theory (DFT) calculations. Tobermorite 11 Å with the chemical formulation of Ca$_{56}$Si$_{8}$O$_{122}$(OH)$_{10}$(H$_2$O)$_{4}$ is used as a model system representing the crystalline structure of calcium silicate hydrate (C–S–H), the main product of cement hydration. Next, the direct effects of intercalation of graphene, GBN, and h-BN on the electronic and mechanical properties of multilayer C–S–H are investigated while considering different proportions of carbon and boron nitride in GBN. The results provide fundamental insights on the application of GBN in ceramics, with several implications on next-generation smart materials with inherent self-sensing, stability, and high mechanical properties.

2. COMPUTATIONAL METHODS

2.1. General DFT Approach and Structural Models. All total-energy calculations were conducted using DFT through the Cambridge Serial Total Energy Package (CASTEP). To calculate the distribution of electron density between atoms, Perdew–Burke–Ernzerhof generalized-gradient approximation (GGA-PBE) was used. The energy cutoff was set to 400 eV for the plane-wave basis, and the Brillouin zone integration was performed on a regular mesh of $6 \times 6 \times 1$ k-points. The full atomic relaxation was achieved when all remaining forces were below 0.01 eV Å$^{-1}$. London dispersion interactions were added to the total bonding energy as proposed by Grimme in the DFT-D method for PBE functional. In order to calculate the electrical and mechanical properties of the unit cell of nanosheet/tobermorite composites, the dimensions of relaxed crystal structure of nanosheet/tobermorite in $\alpha$ and $\beta$ lengths were chosen $6.95$ and $7.38$ Å, respectively. The angle of $123^\circ$ in monoclinic tobermorite closely imitates the $\gamma$ angles of h-BN, GBN, and graphene, that is, $\sim 120^\circ$. This similar geometric pattern imparts great compatibility in the structures of nanosheet and tobermorite during cell optimization, which is then followed by the formation of a stable dual-layer crystal. More details including optimized lattice parameters are discussed in the Supporting Information.

Figure 1 shows the studied models of the bilayer composites in accordance with the different ratios of carbon to boron and nitrogen atoms. In the original model, the 18-atom h-BN nanosheet was confined by the 84-atom tobermorite 11 Å. Next, h-BN atoms were replaced with carbon atoms as needed. GBN models are named using a subscript notation, GBN$_{i-j}$ where $i$ and $j$ describe the share of each nanosheet in the 18-atom hybrid; $i$ is the number of atoms from the graphene structure and $j$ is the share of h-BN atoms. For example, GBN$_{12}$ denotes 6 graphene (carbon) atoms and 12 h-BN atoms. In addition, the nanosheet-tobermorite composite model is included in Figure S1 of the Supporting Information.

2.2. Solubility Calculations. The solubility of the desired 2D platelets was investigated by determining the solvation energy of GBN and comparing it with those in h-BN and graphene. DFT calculations were conducted using the b3LYP hybrid functional; the implicit water environment was accounted for by the conductor-like model scheme. Dispersion correction of Tkatchenko and Scheffler scheme was chosen for b3LYP functional. Vibrational analysis calculations were used to compute important thermodynamic properties such as
enthalpy ($H$), entropy ($S$), free energy ($G$), and heat capacity at constant pressure ($C_p$) as functions of temperature. Using the obtained values for entropy of graphene, GBN, and h-BN, free energy at $T = 298.15$ K was calculated by

$$\Delta G_{\text{exp}}^{298.15K} = \Delta H_{\text{exp}}^{298.15K} - T \Delta S_{\text{exp}}^{298.15K}$$

(1)

Gibbs free energy of solvation, or $\Delta G_{\text{ads}}^\text{solv}$, which is the difference between Gibbs free energy in the secondary and the primary mediums was calculated for each nanosheet; the change in this energy shows relative solubility. The total dipole moment value for GBN is significantly larger than that of graphene, demonstrating a considerable difference in hydrogen atoms on the edges and boron atoms on the surface, which is an influential factor in the solvation of this molecule in aqueous environments. The results are illustrated in Figure 2. Although the demonstrations for h-BN and graphene are verified through previous works, the GBN profile is illustrated for the first time using COSMO analysis.

3. RESULTS AND DISCUSSION


Table 1 lists the Gibbs free energy of solvation for each nanosheet in water; higher values show less tendency toward aqueous solvation. Thus, according to Table 1, the least $\Delta G_{\text{ads}}^\text{solv}$ value belongs to GBN, which highlights the highest solvation tendency, followed by h-BN and graphene. Although the hydrophobicity of graphene and h-BN is already established, it is shown here in terms of the considerable difference in Gibbs energy when compared to the other materials.

Table 2 shows the dipole moment of the studied nanosheet. The charge difference between boron and nitrogen atoms in h-BN ensures a greater dipole moment than the homogeneous graphene. However, the largest dipole moment belongs to the GBN, demonstrating a considerable margin compared to h-BN and graphene. The formation of B–C and N–C bonds alters the charge density distribution on the surface of GBN, causing a relatively strong polarity.

Table 2 lists the Gibbs free energy of solvation for each nanosheet. The change in this energy shows relative solubility.30

$$\Delta G_{\text{ads}}^\text{solv} = \Delta G_{\text{ads}}^\text{water} - \Delta G_{\text{ads}}^\text{air}$$

(2)

Table 1. Predicted Values of Gibbs Free Energy of Solvation for Graphene, GBN, and h-BN in Water

<table>
<thead>
<tr>
<th>nanosheet</th>
<th>$\Delta G_{\text{ads}}^\text{solv}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphene</td>
<td>0.33</td>
</tr>
<tr>
<td>h-BN</td>
<td>-1.10</td>
</tr>
<tr>
<td>GBN</td>
<td>-5.24</td>
</tr>
</tbody>
</table>

nanosheet of graphene, GBN, and h-BN by COSMO.

In view of Figure 2c, GBN is more polarized in terms of electron distribution, which may provide a higher solvation ability in aqueous solutions such as water, which is itself a polar molecule. To further examine this subject, it is worth looking at the electron density of graphene and h-BN in Figure 2a,b. Judging from the color intensity, the polarity is more significant in h-BN, with the electron distribution more leaning toward nitrogen atoms over the whole surface, whereas in the graphene, the structure is more homogeneous in terms of charge, with the internal carbon atoms amassing negative charge, as opposed to the marginal hydrogen atoms with positive charges.

Figure 2d describes the sigma profile of the molecules in aqueous environment. All of the models demonstrate a similar shape, a small peak in the left at approximately $-0.006$ with the other peak close to zero, at the right side of the diagram. Graphene profile does not reach the h-bond regions on both sides, signaling a hydrophobic behavior. In the right side, h-BN shows a behavior similar to graphene. However, the h-BN profile reaches the h-bond receptor region at the left side, making it more solvable than graphene. It can be attributed to the distribution of charge density over h-BN, with the hydrogen atoms on the edges and boron atoms on the surface, both being electrophile species and providing a desirable surface for the electrons. The GBN profile is extended from this profile calculated over all components of the said molecule and displayed against screening charge density.37

We performed Cosmo and Sigma profile analyses to determine the distribution of valence electron, or the distribution of surface charge on the molecule, which is an influential factor in the solvation of this molecule in aqueous environments. The results are illustrated in Figure 2. Although the demonstrations for h-BN and graphene are verified through previous works, the GBN profile is illustrated for the first time using COSMO analysis.

Figure 2. (a–c) Electronic density of the different compounds (the red color and blue one are typical for a region acceptor of positive and negative partial electrostatic charges of water molecule, respectively), and (d) sigma profiles of graphene, GBN, and h-BN by COSMO.
about −0.015 to 0.14, covering more ranges than h-BN and graphene. This indicates that GBN has the potential to form better dispersion in water compared to graphene and h-BN. Essentially, GBN performs similar to h-BN in the left side of the diagram, whereas for the right side, it desires interaction with the positive pole of water (hydrogen atoms) where it reaches 0.014. However, no significant peak is present in the right side, which denies absolute hydrophilic behavior for GBN. Therefore, it can only be stated that GBN is more likely to show a better aqueous dispersion than graphene and h-BN. Overall, GBN shows higher potential for an aqueous solution comparing to both graphene and h-BN, making it the preferred choice for mixing with cement slurry and potential intercalations described next.

3.2. Absorption, Bonding, and Charge Transfer.

Figure 3 shows three 18-atom nanosheets of GBN$_{9-9}$, graphene, and h-BN confined in tobermorite. As an example, Figure 3a demonstrates the structure before absorption (optimization) of the GBN$_{9-9}$ by tobermorite where the main forces present are van der Waals forces. The separation distance is 3.15 Å on each side. Figure 3c,d shows the same structure, GBN$_{9-9}$/tobermorite, after optimization where oxygen atoms act as the nucleophilic sites on the silicate chains attached to the GBN electrophilic sites. The other components of tobermorite, namely, calcium ions, hydroxyl, and water hold their positions relative to that of silicate chains, thus creating a nanosheet/tobermorite composite held together mostly by electrostatic forces.

During the absorption (optimization) phase, covalent bonds are formed between the oxygen atoms present in the silicate chains and the boron and carbon atoms in the nanosheets, reducing the separation distance to ~1.5 Å and subsequently releasing −1.16 and −1.41 eV of energy to form O−B and O−C bonds (Figure 3g). This development of the B−O and C−O covalent bonds can also be assessed from observing the differences in electron densities. Figure 3b,e shows GBN$_{9-9}$/tobermorite before and after optimization. The electron density shifts toward boron and carbon atoms, indicating the creation of covalent bonds between tobermorite and GBN nanosheet. The transferred charge of silicate chains to the nanosheet can be seen clearly in the middle of Figure 3h, creating a monolith chain of GBN and tobermorite. The newly formed covalent bonds result in sp$^3$ hybridization in the GBN, making the GBN electric charge gravitated to the negative side. On the graphene portion of the GBN nanosheet, this covalent bond forms between carbon and the oxygen atoms of the silicate, whereas in the h-BN portion, between boron atoms and oxygen atoms of the silicate. This is also the
case for intercalation of phase pure h-BN and graphene in tobermorite (Figure 3i,j) where the nucleophile oxygens on the silicate chains of tobermorite share electron with the electrophilic carbon and boron atoms on the graphene and h-BN nanosheets, forming covalent bonds between the two structures.

To complement these findings, we determined the in-plane bond length distributions of each of the nanosheets (h-BN, graphene, and GBN_{9-12}) before and after absorption on tobermorite (Figure S3). The average (maximum) in-plane bond length of h-BN, graphene, GBN_{9-12} increased 2.7, 2.9, and 2.4% (7.5, 8.2, and 7.5%), respectively, after absorption, because of the transformation of the sp² hybridization into sp³. Although GBN demonstrated the most stable behavior as determined by the minimal changes in the “average” bond length, the maximum bond lengths followed similar patterns akin to h-BN and graphene, clearly affecting the valence electron density of the composites.

Figure 4 demonstrates the energy released when the nanosheet is absorbed by tobermorite. The least absorption energy belongs to the h-BN/tobermorite with −12 eV, and the most to graphene/tobermorite with −13.5 eV. Generally, by replacing the boron and nitrogen atoms with carbon, C−O bonds replace B−O bonds, becoming more structurally stable, consistent with Figure 5g. The formation of these covalent bonds with different degrees of release energy influences the electrical and mechanical properties of the nanocomposites, described next.

3.3. Electrical Behavior. 3.3.1. Conductivity. Figure 5a shows the status of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for the h-BN, GBN, and graphene structures. The HOMO orbitals are negatively charged on nitrogen and carbon atoms in h-BN and GBN. LUMO orbitals contain positive or no charge on boron and carbon atoms in h-BN, GBN, and graphene. Figure 5b highlights the differences between h-BN and the rest of the nanosheets, that is, GBN_{9-12} and graphene. The band gap—a key attribute of electrical properties—is 4.28 eV for h-BN, 0.0 eV for graphene, 0.3 eV for GBN_{9-12}, 0.33 for GBN_{9-9}, and 0.0 eV for GBN_{12-6} in line with previous works.12,39,40 Regarding the identical band gaps for graphene and GBN_{12-6}, the following deserve attention: generally, the band gap decreases with the increase in the number of carbon atoms, as expected. However, other parameters such as structural type (armchair/zigzag) and connectivity and the location of carbon and nitrogen/boron atoms are also influential.12 As for the different fusion patterns of graphene and h-BN, band gap states are brought in Figure S4 in the Supporting Information.

To probe the effect of above nanosheets on the band gap of the tobermorite, Figure 6a−c illustrates the relaxed structures of h-BN/tobermorite, graphene/tobermorite, and GBN_{9-9}/tobermorite. Although oxygen atoms are bonding covalently with boron atoms in h-BN, there are van der Waals interactions with nitrogen atoms in h-BN, at an atomic distance of 2.4 Å. However, covalent interactions with oxygen atoms of the tobermorite structure occur around 1.5 Å in GBN and graphene. Figure 6d depicts the band structure of fully insulator tobermorite 11 Å with the valence band maximum (VBM) and the conduction band minimum (CBM) appearing at the G point. The electrically insulating behavior in this structure is well known via several experiments and studies on cement and C−S−H (e.g., ref 42). Also, Figure 6d represents partial density of states for tobermorite 11 Å, demonstrating the contribution of oxygen atoms, which are nucleophile, in the HOMO region compared to the other species. This is in contrast to the calcium ions which have the greatest impact in the LUMO area because of the positive charge. The VBM located in the LUMO area is far from the Fermi level and the
generated band gap is 4.35 eV. This band gap is a simple representation that transferring electrons from HOMO to LUMO region is near impossible without external interference.

Compared to graphene, the lack of covalent bonding between nitrogen (not boron) and oxygen of silicate reduces the number of available sites on the surface of the h-BN. Simply put, the absorption of oxygen of the silicon tetrahedra on a graphene platelet does not have this limitation. Our calculations on h-BN/tobermorite show a band gap of \( \sim 2.61 \) eV (Figure 6e). This is somewhat nonintuitive. As discussed earlier, tobermorite and h-BN are both wide band gap materials with 4.35 and 4.28 eV band gaps, respectively. However, their intercalated composite demonstrates a band gap that is almost half of those of parent materials. This is because of the covalent B–O bonds in the h-BN/tobermorite. More precisely, the contributing factor is the decrease in the bond length and release of the electrons in the boundary between tobermorite and h-BN which is trespassed by the B–O bond. Akin to tobermorite, the CBM and VBM for h-BN/tobermorite are both located at the \( G \) point in the Brillouin zone.

The hybrid graphene/tobermorite behaves much like a p-type semiconductor material (Figure 6f). Further analysis of the wave function indicates that the VBM and CBM near \( FQ \) points are mainly provided by carbon p\(_z\) orbitals, which is capable of creating a band gap of 0.43 eV for the graphene/tobermorite structure. The addition of graphene to tobermorite alters significantly its electrical behavior and produces a semiconductor ceramic. This interesting quality is via a decrease in the band gap, which results in a more feasible electron transfer from HOMO to LUMO orbitals.

By changing the ratio of h-BN to graphene in the hybrid nanosheet, its electrical properties changes, allowing the creation of a structure with tailored electrical properties. Figure 6g–i shows the band structures and electron density of states of composites made of tobermorite and GBN\(_{6-12}\), GBN\(_{9-9}\), and GBN\(_{12-6}\). An interesting point in the electrical properties of GBN/tobermorite composites is the dramatic change in the electrical properties by addition of GBN with minimal carbon content. The model with the least carbon, GBN\(_{6-12}\)/tobermorite, has a direct gap and is a semiconductor characterized by a band gap of 0.86 eV (from \( F \) point to \( Q \) point), as depicted in Figure 6g. Addition of GBN\(_{12-6}\)/tobermorite.
regular crystal lattice of tobermorite produces a semiconductor nanocomposite. This is because GBN contributes electrons with high energy levels to the GBN/tobermorite composite band gap; thereby, electrons can be easily excited into the conduction band. Following this mechanism, an increase in the number of carbon atoms in the GBN structure moves the band gap of GBN/tobermorite composites closer toward the graphene/tobermorite composite band gap, as intuitively expected. The increase in the number of carbon atoms can transfer electrons from the highest-energy state in the VBM to the lowest-energy state in the CBM without a change in the GBN/tobermorite crystal. Therefore, the band gaps in the GBN$_{6}$/tobermorite structure and GBN$_{12}$/tobermorite are reduced to 0.66 and 0.55 eV, respectively (Figure 6h).

Figure 7 summarizes the band gap energies of the studied nanosheets/tobermorite composites with respect to number of carbon atoms in the GBN of GBN/tobermorite composites.

**Figure 7.** Band gap energy vs the number of carbon atoms in GBN of GBN/tobermorite composites.

![Graph showing band gap energy vs number of carbon atoms in GBN](image)

Table 3. Mechanical Properties of Tobermorite and Nanosheet-Reinforced Tobermorite

<table>
<thead>
<tr>
<th>Combination</th>
<th>$K_{VRH}$ (GPa)</th>
<th>$G_{VRH}$ (GPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>T$_{11}$</td>
<td>63.45</td>
<td>33.21</td>
<td>84.82</td>
<td>0.277</td>
</tr>
<tr>
<td>T$_{11}$ + h-BN</td>
<td>95.42</td>
<td>43.17</td>
<td>112.53</td>
<td>0.303</td>
</tr>
<tr>
<td>T$<em>{11}$ + GBN$</em>{6-12}$</td>
<td>93.49</td>
<td>45.14</td>
<td>116.64</td>
<td>0.292</td>
</tr>
<tr>
<td>T$<em>{11}$ + GBN$</em>{9-9}$</td>
<td>94.47</td>
<td>45.58</td>
<td>117.79</td>
<td>0.292</td>
</tr>
<tr>
<td>T$<em>{11}$ + GBN$</em>{12}$−6</td>
<td>98.55</td>
<td>47.42</td>
<td>122.59</td>
<td>0.292</td>
</tr>
<tr>
<td>T$_{11}$ + graphene</td>
<td>100.89</td>
<td>49.34</td>
<td>127.27</td>
<td>0.289</td>
</tr>
</tbody>
</table>

$^{a}$T$_{11}$: tobermorite 11 Å.

**3.4. Mechanical Behavior and Strain-Dependent Band Gap.**

3.4.1. Elastic Regime. First, we investigated Young’s modulus of tobermorite composites intercalated by h-BN, GBN$_{6-12}$, GBN$_{9-9}$, GBN$_{12-6}$, and graphene (Table 3). To obtain average elastic properties of this low-symmetry bilayer crystals, we initially constructed the triclinic elastic tensors of these crystals, following the procedures described in the Supporting Information and ref 44. Next, we used conventional Voigt, Reuss, and Hill (VRH) approach to determine the lower and upper bounds for the average shear modulus ($G$) and average bulk modulus ($K$). Having these values, the equivalent isotropic Young’s modulus ($E$) and Poisson’s ratio ($\nu$) were estimated via VRH approximation. Table 3 shows that the presence of h-BN, GBN, and graphene in tobermorite enhances significantly the elastic properties of the composites. Young’s modulus of tobermorite is 84.82 GPa, which increases by 32, 37, 39, 44, and 50% via intercalation of h-BN, GBN$_{6-12}$, GBN$_{9-9}$, GBN$_{12-6}$, and graphene, respectively.

This improvement traces back to the strong covalent bonding discussed earlier. Moreover, these intermittent covalent bondings hinged on repetitive C and/or B atoms induce several weak local buckling (deformation) in the h-BN, GBN, and graphene sheets. The formation of B–O and C–O bonds at certain spots imposed by periodicity of silicates in tobermorite leads to wrinkling in the nanosheets. This geometrical deformation, combined with the changes in hybridization from sp$^2$ to sp$^3$, weakens the nanosheet structure, yet the remaining C–C and B–N bonds are still sufficient to provide significant reinforcement for the tobermorite matrix (Table 3).

3.4.2. Inelastic Regime. The main task of the GBN nanosheet fillers is typically introducing tunable electrical properties while mechanically reinforcing the ceramics. Thus, it will be interesting to determine the strain-dependent band gaps. Figure 8a compares the stress–strain diagrams for the pristine tobermorite and the GBN$_{6-9}$/tobermorite composites, as a representative model. Tensile strain is imposed along the out-of-plane direction, which is the most vulnerable mechanical direction. The maximum stress is 5.76 GPa at 0.175 strain. Figure 8b clearly marks the interaction zone as the weak link in the structure (red clouds). As the strain accumulates, two half cells of pristine tobermorite drift apart which weakens the electrostatic interactions, replacing them with van der Waals forces. In contrast, in the GBN$_{6-9}$/tobermorite composites, GBN$_{6-9}$ fills this vulnerable gap between the two half cells. For this particular composite, the stress strain plot shows a higher slope (thus higher Young’s modulus) as well as a higher maximum stress of 6.58 GPa at 10% strain.

The higher Young’s modulus and strength are attributed to the formation of multiple B–O and C–O bonds between the two structures, connecting more coherently the two-half cells of tobermorite. Although the addition of nanosheets enhances the interactions between the upper and lower cells of the tobermorite, the rupture occurs in these newly formed C–O and B–O bonds which are the only main bridges between the upper and lower half cells (Figure 8c). Figure 8d shows the band gap of pristine tobermorite and GBN$_{6-9}$/tobermorite calculated at the different strains. The overall pattern for both structures suggests that applying tensile strain increases the
band gap. However, in the case of GBN$_{a,g}$/tobermorite, an initial drop in the band gap is observed at 5% strain, which can be attributed to the spot where the valence electrons are partially released from the calcium ions in the tobermorite structure but are still able to travel within the whole structure. This may imply that perhaps the best electrical performance of the composites is in the elastic zone from 0 to 5% strain. Although the overall pattern of the strain-dependent band gap is expected to hold true for other GBN/tobermorite structures, more studies are needed in the future to identify anomalies and potential synergies as noted above (e.g., 5% strain).

4. CONCLUSIONS

Using extensive DFT calculations, this work studied the electrical and mechanical properties of intercalated GBN/tobermorite as representative ceramic composites. Though both graphene and h-BN are hydrophobic, GBN hybrids demonstrate good solvation and dispersity in water as observed by more polarity in electron distribution, negative value for Gibbs free energy and COSMO analysis, making GBN a more preferred choice for slurry preparation and resultant homogeneous cementitious mixtures, compared to hBN and graphene.

A key trait of such intercalated composites is the formation of covalent C–O and B–O bonds between the nanosheets and tobermorite matrix. These covalent bonds change the hybridization of GBN from sp$^2$ to sp$^3$, which impart significant mechanical and electrical alterations to the composite such as higher Young’s modulus, strength, and ductility as well as a sharp decline in the band gap. The large band gap of tobermorite at $\sim$4.5 eV reduced to 0.624 eV when intercalated by a fused hybrid GBN nanosheet of equal parts of graphene and h-BN. Further, though both tobermorite ceramic and h-BN are wide band gap materials, their intercalated composite becomes a p-type semiconductor with almost half of the band gap compared to those of the parent materials. This counterintuitive result is due to the formation of covalent O–B bonds between the two structures and the resulting electron release in the vicinity of the interfacial region. This phenomenon imparted a complex behavior when subjected to tensile strain, that is, pristine tobermorite showed a steady increase in band gap by increasing tensile strain, whereas the GBN/tobermorite composite demonstrated an initial drop in band gap before saturation. However, in the elastic regime, conductivity grows with increasing strain, demonstrating promises for applications for self-sensing and structural health monitoring.

Unlike 1D fibers such as CNT or BNNT, 2D materials such as ternary GBN nanosheets not only display double surface area per unit mass but also exhibit great solubility and dispersion in water, making it perfect for mixing, bridging, and reinforcement at smallest possible scales of the host matrix. This tactic in intercalating ultrathin, tunable, and water-soluble 2D materials in matrices holds good promises for synthesizing next-generation bilayer materials with multifunctional properties such as electrical and mechanical properties on demand. Broadly, the concepts, methods, and strategies of this work can have implications on other ceramic-based materials to intercalate a set of other emergent (ternary) 2D mono- and few-layer sheets—for example, composed of molybdenum disulfide, niobium diselenide, and layered double hydroxides—for a bottom-up design of tunable multifunctional composites.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b19409.

Cell parameters of various structures, and further details of DFT calculations, mechanical property predictions, bond length analysis, dipole moments, and effect of B/N ratios (PDF)
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