ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2021, Vol. 95, Suppl. 2, pp. S331–S337. © Pleiades Publishing, Ltd., 2021.

PHYSICAL CHEMISTRY OF NANOCLUSTERS AND NANOMATERIALS

Induced Metals on BN–Nanotube by DFT/EPR Methods

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Received September 15, 2020; revised September 15, 2020; accepted November 21, 2020

Abstract—In this study, the isolated boron nitride nanotube has been characterized using the B3LYP exchange-correlation functional of theory by electron paramagnetic resonance of EPR3 basis set. Then the effect of metals such as Li, Na, K, Be, Mg, and Ca inside BN–nanotube has been investigated. Nuclear Magnetic Resonance (NMR) parameters such as, isotropic chemical shielding, anisotropic chemical shielding, asymmetry, chemical shift anisotropy and total atomic charges of BN–nanotube including of metal systems have been calculated with GIAO approximation. It has been shown that the behavior of chemical shift tensor components (isotropic and anisotropic), chemical shift anisotropy, asymmetry and devotion depending on the metal that locating at the center of BN–nanotube that some of periodic transformations. Also, Atomic charge have considered to full alternation B, N and metal atoms in BN–nanotube determined the active sites of structures. Thermo chemical functions of relative enthalpy (ΔH), entropy (ΔS) and free Gibbs energy (ΔG) have been calculated. Our investigation exhibited that some metal atoms can strongly bind to the BN–nanotube to enhance the potential electronic molecular effects of these compounds for various applications.

Keywords: BN–nanotube, metal, NMR, thermochemical

DOI: 10.1134/S003602442115019X

INTRODUCTION

Boron nitride (BN) is isoelectronic to a similarly structured carbon lattice and thus exists in various crystalline forms. Its thermal and chemical stability is superior to diamond. The rare wurtzite BN-modification is similar to lonsdaleite and may even be harder than the cubic form [1].

Boron nitride nanotubes were theoretically predicted in 1994 and experimentally discovered in 1995 [2, 3].

Most experimental and theoretical researches of metal-nanotube interactions have been particular to the carbon nanotube with transition-metal systems. According to the WU Haishun et al. studies into $(BN)_n$ cages [4], it is found that among several isomers of BN structures the isomers without direct B–B and N–N bonding are more stable than other structures.

The metal component can be a single atom, a metal cluster, or a planar metal surface [5–8]. Boron nitride nanotubes (BN), was another tubular nanomaterial which synthesized after the discovery of the carbon nanotubes. BN–nanotubes have also many unique physical and mechanical properties. For example this compounds have strong hardness, high thermal stability, and chemical inertness [9–12].

Today, fewer research work have been done on the BN–nanotube-metal systems, compared to the amount of work reported on the carbon nanotube–metal systems. One known resent about the interaction between a BN nanostructure and metal is that the graphite like BN surface has much more problem to wet by metals than the carbon graphite surface. Recently, several experimental works have been made to fill the BN–nanotubes with 3*d* transition metals, such as Fe–Ni (Invar alloy), Co, Mo, Ni, and $NiSi_2$ [13–17].

On the theoretical side, several studies on the filling the BN–nanotubes with transition metals have been reported, wherein half-metallic behavior has been seen in some of these systems [18, 19].

Boron nitride nanotubes (BNNTs) made of alternating boron and nitrogen atoms in graphite like network, and are polar in nature due to large charge on boron and nitrogen atoms. Hence, electrostatic interactions are anticipated to play a significant role in determining the elastic properties of BNNTs [20, 21]. The mechanical and wear-resistant properties of both materials are the same for example; CNTs are either metals or semiconductors [22].

Depending on their chirality's while BNNTs are always semiconductors with the gap (5.5 eV) almost

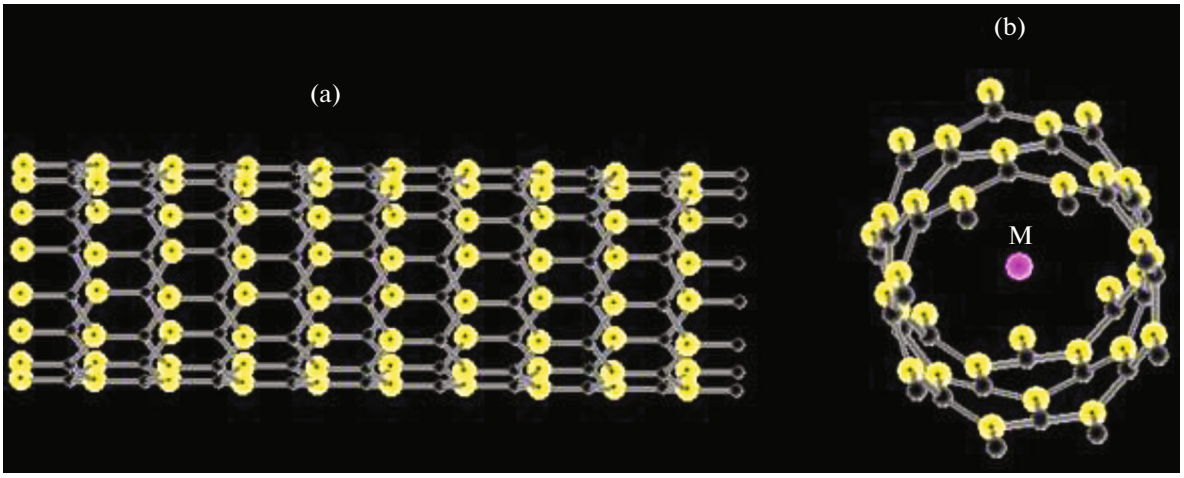

Fig. 1. Optimized (a) boron nitride (BN) nanotube, (b) BN–M nanotubes (M = Li, Na, K, Be, Mg, Ca) using by DFT/EPRIII/LANL2DZ basis sets.

independent of the nanotube chirality's and its diameter [23, 24]. As hexagonal. Boron nitride (h-BN) is very resistant to oxidation, BNNTs which holding these properties are suitable for shielding and coating at the nanoscale. In spite of these singularities, BNNTs have received so little attention compared to CNTs due to various difficulties in their reproducible and efficient synthesis [25–27].

Actually the BNNT consists of two different atomic species implies that the synthesis of BNNTs is more problematic than the synthesis of monatomic CNTs; also chemical reactions might be done. CNTs are typically synthesized from hydrocarbon initially and according to present theoretical finding of the CNT formation process, single carbon atoms diffuse in or on a metal nanoparticle, forming graphitic networks that finally gives rise to the appearance of a CNT [28–32].

Thus, these ideas are relevant to the growth of BNNTs; it becomes important to understand the factors that determine whether single nitrogen and boron atoms, or N_2 molecules and B clusters diffusing on a catalytic surface to formation of BN structures.

In this paper, we have studied of the interaction between the BN nanotube and metals and two group (IA and IIA) metals using spin-polarized density functional theory (DFT). Our calculations showed that some metal atoms can strongly bind to the BN–nanotube. This may lead to potential applications in future molecular electronics.

COMPUTATIONAL METHODS

Density functional theory (DFT) quantum calculation was performed using Gaussian 98 program package on structure of boron nitride nanotube including of metals [33]. The optimized structures have been measured by nuclear magnetic resonance (NMR) parameters using LANL2DZ basis set for metals and EPRIII for boron and nitrogen atoms (Fig. 1).

The nuclear magnetic resonance (NMR) parameters were calculated using the gauge-including atomic orbital (GIAO) approximation at B3LYP level of theory. The calculation methods used are the ab-initio (from first principles) Hartee–Fock or density functional calculations [34–37]. The first method solves all of the electronic Schrödinger equation in the absence of any magnetic field. The density functional method was allowed to change with the applied of a magnetic moment and a static external magnetic field. The zero order and first order density matrices are used to obtain the diamagnetic and paramagnetic terms, respectively. The integrity of these calculations depends on the level of theory that be used, the basis set employed the metal putting at the center of nanotube and the structure of molecule. Gaussian basis sets are employed as the basis functions to match the electronic orbital in a molecule [38, 39].

Table 1. Bond length (Å) measured for boron nitride nanotube including of the metals using by DFT/LANL2DZ basis set

Metal	B or N metal						
	B4-M	B5-M	N7-M	N9-M	B12-M	B13-M	N17-M
Li	4.43	4.42	5.58	3.75	4.56	4.84	4.28
Na	4.80	4.38	5.77	4.28	4.88	4.80	4.28
K	5.37	7.84	6.87	4.58	5.52	6.47	5.33
Be	3.61	2.08	4.38	3.54	4.05	3.40	3.23
Mg	4.38	3.73	5.27	3.79	4.36	4.28	3.76
Ca	5.03	7.63	6.46	4.07	4.71	4.97	4.23

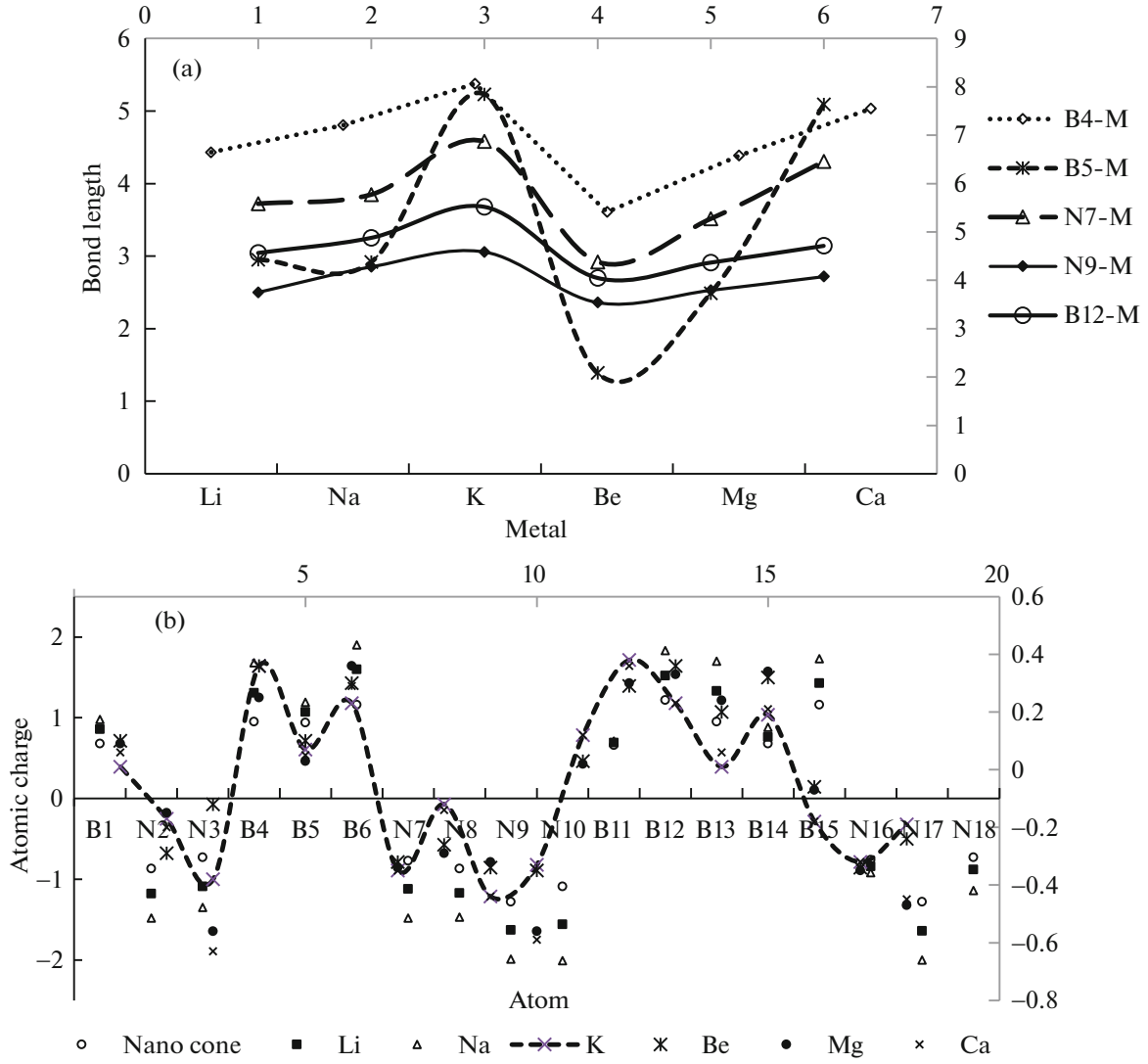

Fig. 2. Calculated (a) bond length (Å), (b) atomic charge transfer of boron nitride (BN), BN–Li, Na, K and BN–Be, Mg, Ca nanotubes using by DFT/EPRIII/LANL2DZ basis sets.

Also the Gaussian program is used to investigate thermo chemical properties of isolated BN–nanotube and boron nitride nanotube including of two groups of metals (Li, Na, K, Be, Mg, and Ca) such as relative enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG).

RESULTS AND DISCUSSION

In this study the geometry coordination of boron nitride nanotube has been calculated and then Li, Na, K, Be, Mg, and Ca metals as the particular cases were considered to place in the center of BN–nanotube and bond length (Å) properties of boron nitride nanotube including of the metals have been measured (Fig. 1 and Table 1).

Both experiment and theory suggest that the interaction between metals and BN–nanotubes is very significant. Optimization of boron nitride nanotube has been applied using by B3LYP method with EPR3 basis set for B and N atoms and LANL2DZ basis set for the metals.

The interaction of Li, Na, Be, Mg, and Ca metal atoms with BN–nanotube showed that the sharp picks in bond length curves were belonged to K and Ca (Fig. 2).

Therefore, maximum and minimum interactions were between the metals and N_9, N_7 atoms of BN–nanotube.

In addition total atomic charges of BN–nanotube and BN–M (M = Li, Na, K, Be, Mg, Ca) have shown that the N atoms had the most charge distribution (Table 2). In BN– and BN–M–nanotubes, the most negative charge values were belonged to N_9 and N_{10} (Fig. 2).

The results of ab initio calculations of NMR chemical shift values with GIAO approximation of σ_{iso}, σ_{aniso},

Table 2. Nuclear magnetic resonance parameters (ppm) of isotropic shielding (σ_{iso}), anisotropic shielding (σ_{aniso}), asymmetric (η), and chemical shift (δ) of boron nitride (BN), BN–Li, Na and BN–Be, Mg, Ca nanotubes using by DFT/EPRIII/LANL2DZ basis sets

Atom	σ_{iso}	σ_{aniso}	η	δ	Charge	σ_{iso}	σ_{aniso}	η	δ	Charge	σ_{iso}	σ_{aniso}	η	δ	Charge
	BN					BN–Li					BN–Na				
B1	75.33	166.81	0.07	111.21	0.68	83.41	170.23	0.20	113.48	0.18	82.71	169.51	0.17	113.01	0.12
N2	151.43	90.86	0.96	–61.69	–0.87	146.47	71.301	0.57	–60.26	–0.31	145.66	74.37	0.60	–66.5	–0.30
N3	66.17	321.77	0.48	214.51	–0.73	100.45	243.74	0.49	162.49	–0.36	86.26	268.98	0.35	179.32	–0.26
B4	88.53	34.29	0.71	22.86	0.95	84.87	54.347	0.58	36.23	0.36	85.99	52.15	0.93	34.77	0.37
B5	59.15	149.45	0.22	99.64	0.94	44.11	94.935	0.29	–98.26	0.13	42.47	95.88	0.38	–98.54	0.12
B6	67.98	56.95	0.81	–42.05	1.16	83.02	34.088	0.20	–37.91	0.44	86.57	39.07	0.48	–38.59	0.30
N7	139.97	77.63	0.35	51.75	–0.77	154.27	93.898	0.98	62.60	–0.35	155.24	91.10	0.64	60.73	–0.36
N8	151.43	90.86	0.92	–64.68	–0.87	146.51	78.033	0.51	–68.78	–0.30	145.69	74.38	0.60	–66.54	–0.30
N9	63.44	128.88	0.74	85.92	–1.28	85.29	126.65	0.74	–96.53	–0.35	78.45	118.65	0.85	–92.63	–0.36
N10	–27.89	194.35	0.66	–164.64	–1.09	100.55	223.92	0.17	149.28	–0.47	94.56	234.34	0.30	156.23	–0.45
B11	61.84	191.03	0.20	127.35	0.66	75.60	179.03	0.18	119.35	0.03	75.66	179.75	0.25	119.84	0.02
B12	63.77	61.67	0.69	–48.63	1.22	76.47	53.14	0.55	–45.69	0.30	77.70	50.28	0.47	–44.78	0.31
B13	88.53	34.29	0.71	22.86	0.95	84.87	52.28	0.85	34.86	0.38	86.00	52.12	0.93	34.75	0.37
B14	75.33	166.81	0.06	111.21	0.68	82.92	170.57	0.09	113.71	0.08	82.71	169.51	0.17	113.01	0.12
B15	67.98	56.95	0.80	–42.05	1.16	86.96	31.66	0.21	–34.70	0.27	86.60	39.07	0.48	–38.58	0.30
N16	12.63	350.60	0.04	233.73	–0.76	25.82	376.71	0.31	251.14	–0.08	26.69	374.80	0.11	249.87	–0.08
M						92.69	11.02	0.91	7.35	0.56	–0.32	8.02	0.43	5.34	0.72
	BN–Be					BN–Mg					BN–Ca				
B1	80.83	161.31	0.06	107.53	0.10	78.29	175.54	0.27	117.02	0.09	77.05	173.19	0.23	115.46	0.06
N2	120.12	74.18	0.57	–62.69	–0.29	132.72	78.54	0.61	–64.72	–0.15	121.21	174.92	0.13	116.61	–0.20
N3	156.85	34.59	0.62	–28.41	–0.12	171.85	19.87	0.39	–18.99	–0.56	140.54	101.08	0.70	–79.26	–0.63
B4	75.51	58.07	0.66	–46.66	0.36	90.45	40.20	0.45	–36.90	0.25	80.36	185.50	0.21	123.66	0.36
B5	77.44	45.95	0.20	–50.74	0.10	–0.77	302.84	0.32	201.89	0.03	–0.45	301.40	0.33	200.93	0.05
B6	82.49	165.95	0.05	110.63	0.30	85.01	34.93	0.70	–27.36	0.36	93.61	47.40	0.43	–44.23	0.29
N7	107.43	104.63	0.67	–83.34	–0.32	88.14	264.33	0.60	176.22	–0.34	88.77	262.68	0.61	175.12	–0.35
N8	131.89	230.45	0.26	153.63	–0.26	129.76	144.20	0.29	96.13	–0.29	137.07	49.88	0.25	–52.90	–0.14
N9	76.49	200.41	0.65	–162.04	–0.34	139.22	135.24	0.09	90.16	–0.32	166.88	44.05	0.11	–52.58	–0.44
N10	216.18	65.60	0.69	43.73	–0.35	102.10	199.47	0.85	132.98	–0.56	150.42	134.46	0.89	89.64	–0.59
B11	77.86	167.85	0.27	111.90	0.03	80.01	170.25	0.17	113.49	0.02	80.53	172.46	0.16	114.97	0.12
B12	73.49	54.79	0.46	–49.97	0.29	92.17	24.58	0.29	–25.26	0.30	92.29	24.90	0.69	–19.61	0.36
B13	73.12	91.57	0.84	61.04	0.36	80.85	172.74	0.23	115.16	0.33	89.71	40.95	0.51	–35.97	0.23
B14	95.53	150.37	0.09	100.24	0.20	80.30	171.66	0.23	114.44	0.24	78.23	182.24	0.27	121.49	0.06
B15	87.07	166.70	0.03	111.14	0.32	86.13	55.14	0.52	–48.30	0.34	88.26	24.93	0.28	–25.94	0.21
N16	36.80	366.34	0.18	244.22	–0.06	119.72	128.67	0.94	85.78	–0.07	122.31	137.84	0.91	91.89	–0.18
M	114.60	13.45	0.36	8.96	0.25	0.96	5.35	0.13	–6.29	1.16	123.69	9.77	0.61	–8.09	1.58

δ, and η parameters for BN and BN–M nanotubes have been given in Table 2.

Calculated isotropic chemical shielding parameters of Li, Na, K nuclei have almost similar behaviors in all of the methods and BN–nanotube including metal atoms inside them have maximum σ_{iso} values in N2, N7, and N8 comparison to other atoms and minimum value was belong to N16 (Fig. 3a).These results are in agreement with the results belonged to isolated BN–nanotube.

Very different bonding strong covalent within the planes where boron and nitrogen atoms are covalently bonded and weak between them causes high anisotropy of most properties of boron nitride nanotubes (Table 2).

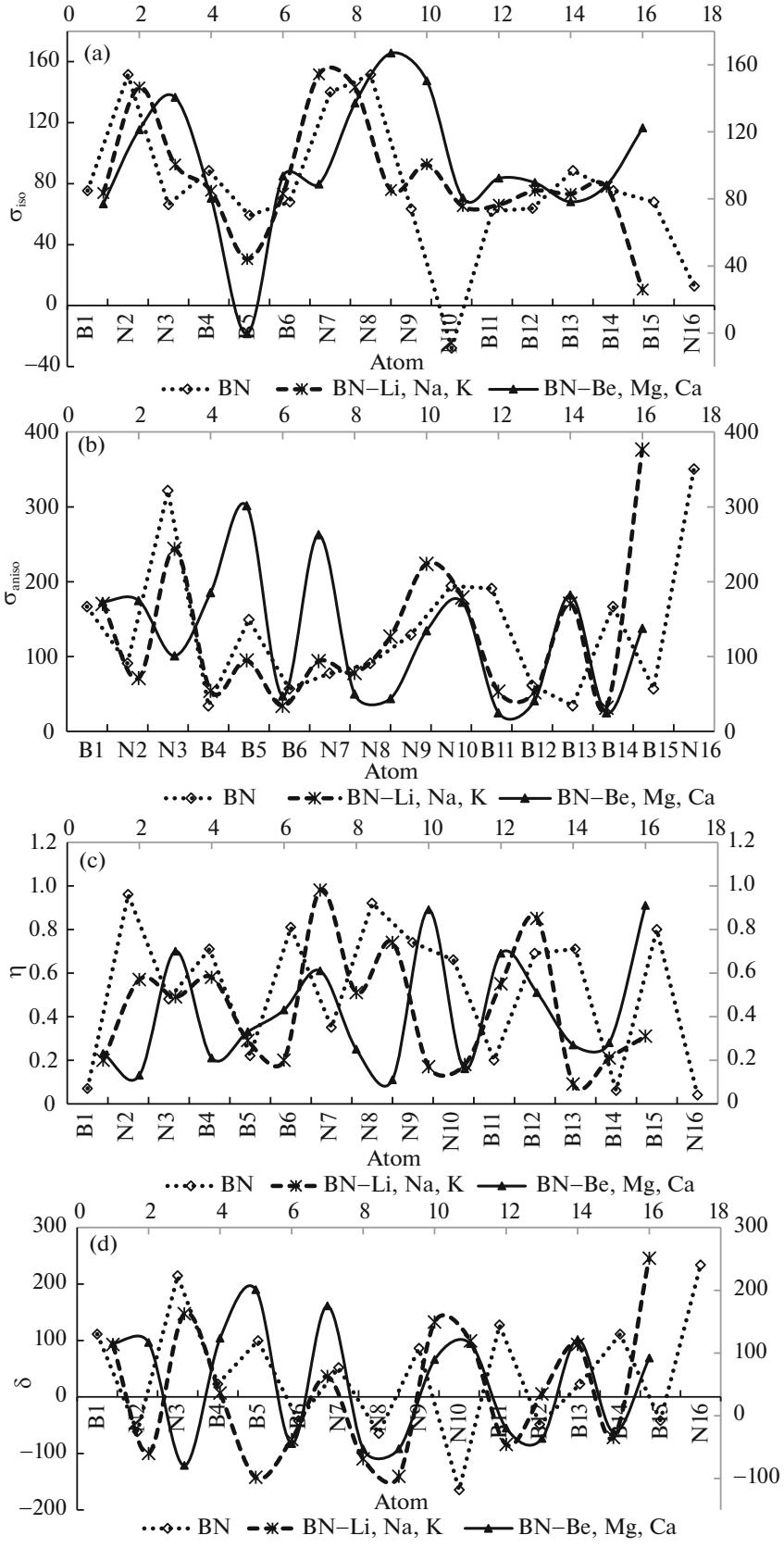

Fig. 3. Nuclear magnetic resonance parameters (ppm) of **(a)** isotropic shielding (σ_{iso}), **(b)** anisotropic shielding (σ_{aniso}), (c) asymmetric (η), and **(d)** chemical shift (δ) of boron nitride (BN), BN–Li, Na, K and BN–Be, Mg, Ca nanotubes using by DFT/EPRIII/LANL2DZ basis sets.

Table 3. Thermodynamic properties of relative, enthalpy, entropy and Gibbs free energy for boron nitride (BN), BN–Li, Na, K and BN–Be, Mg, Ca nanotubes using B3LYP exchange-correlation functional of theory by EPRIII and LANL2DZ basis sets at different temperatures

Thermodynamic properties	ΔH, kcal/mol						ΔS, kcal/(K mol)						ΔG, kcal/mol					
sample	T																	
	294	296	298	300	302	304	294	296	298	300	302	304	294	296	298	300	302	304
BN	0.00	0.09	0.20	0.29	0.39	0.49	0.00	0.33	0.69	1.00	1.33	1.66	0.00	–0.19	–0.41	–0.59	–0.79	–0.99
BN–Li	0.00	0.10	0.21	0.31	0.42	0.52	0.00	0.35	0.72	1.05	1.40	1.75	0.00	–0.20	–0.42	–0.61	–0.82	–1.03
BN–Na	0.00	0.10	0.21	0.30	0.41	0.51	0.00	0.34	0.71	1.03	1.38	1.72	0.00	–0.21	–0.43	–0.62	–0.83	–1.05
BN–K	0.00	0.11	0.24	0.34	0.46	0.58	0.00	0.38	0.80	1.16	1.54	1.92	0.00	–0.25	–0.51	–0.75	–1.00	–1.25
BN–Be	0.00	0.10	0.21	0.30	0.40	0.51	0.00	0.34	0.71	1.02	1.36	1.70	0.00	–0.19	–0.40	–0.58	–0.78	–0.98
BN–Mg	0.00	0.10	0.21	0.30	0.41	0.51	0.00	0.34	0.71	1.03	1.37	1.71	0.00	–0.19	–0.40	–0.59	–0.79	–0.99
BN–Ca	0.00	0.10	0.22	0.32	0.43	0.54	0.00	0.36	0.76	1.09	1.46	1.82	0.00	–0.22	–0.47	–0.68	–0.91	–1.14

The variation of anisotropic chemical shielding (σ_{aniso}) considering to different metals (Li, Na, K, Be, Mg, and Ca) was less than isotropic chemical shielding (σ_{iso}) parameter (Fig. 3b). Respecting more of metals maximum value of σ_{aniso} was belong to N10 that was comparable with σ_{iso}.

Chemical shift (δ) and asymmetry (η) parameters had the are the same behaviors chemical shielding anisotropy that was indicated (Figs. 3c, 3d).

So with putting Li and Na in BN–nanotube the maximum value was belonged to B13 and for K this maximum shift to N3, N9, and B12 with replacing second groups of metals this parameter transferred too. BN–M-nanotubes had a maximum asymmetry on N2, N8 and B13, B15 similar to Li and Na. By replacing the Mg at the center of BN–nanotube rested the maximum point of asymmetry on N8, N16. Also, by substituting of Ca at the center of BN–nanotube N16 and N2 had maximum values (Fig. 3d).

Boron nitride nanotubes show remarkable chemical and thermal stabilities which are stable to decomposition in temperatures up to 1000°C in air, 1400°C in vacuum, and 2800°C in an inert atmosphere [40].

Because of excellent thermal and chemical stability of boron nitride nanotubes, they are traditionally used as parts of high-temperature equipment and they have a great potential in nanotechnology.

Similar to other BN forms, BN–nanotubes are more thermally and chemically stable than carbon nanotubes, which favors them for some applications.

Structurally, it is a close analog of the carbon nanotube, namely a long cylinder with diameter of several to hundred nanometers and length of many micrometers, except carbon atoms are alternately substituted by nitrogen and boron atoms. However, the properties of BN–nanotubes are very different: whereas carbon nanotubes can be metallic or semiconducting depending on the rolling direction and radius, a BN–nanotube is an electrical insulator with a band gap of ~5.5 eV, basically independent of tube chirality and morphology [41]. In addition, a layered BN–structure is much more thermally and chemically stable than a graphitic carbon structure [42].

In this study, we have seen the effect of temperature on BN–nanotube is among the electric conductivity of Li, Na, K, Be, Mg, and Ca metals with thermodynamic properties.

The optimized structures have been investigated the relative Gibbs free energy, enthalpy and entropy on have been considered in different temperatures (294, 296, 298, 300, 302, and 304 K) using B3LYP exchange-correlation functional of theory by EPRIII and LANL2DZ basis set for boron nitride (BN), BN–Li, Na, K and BN–Be, Mg, Ca nanotubes and systems has been stabilized according to the $\Delta G = \Delta H - T\Delta S$, equation (Table 3) [43].

In basis on above equation for isolated BN–nanotube. The Gibbs equation obtained of Fig. 4 was $\Delta G = -0.099\Delta S + 29.106$ with $R^2 = 0.9996$.

The thermo chemical functions have been indicated that with increasing of temperature the stability will be enhanced.

Citing the metal atoms at the center of BN–nanotube changed thermo chemical function values and optimization energy. With placing the Li, Na, and K atoms into BN–nanotube, calculations have been resulted the relative Gibbs free energy as $\Delta G = 30.241 - 0.1029T$ with $R^2 = 0.9998$ (Fig. 4).

Regarding to above equation, it is found that the enthalpy and entropy of BN–Li, Na, K are more than isolated BN–nanotube (Table 3).

In addition that the equation of BN–nanotube-Be, Mg, Ca is $\Delta G = 33.516 - 0.114T$ with $R^2 = 0.9997$ that

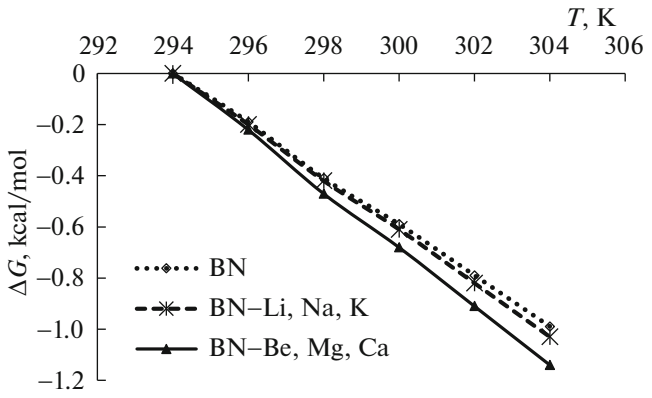

Fig. 4. The effect of temperature (294, 296, 298, 300, 302, and 304 K) on the relative Gibbs free energy for boron nitride (BN), BN–Li, Na, K and BN–Be, Mg, Ca nanotubes using B3LYP exchange-correlation functional of theory by EPRIII and LANL2DZ basis sets.

shows the stability by the adding second groups of metals stability will be increased (Fig. 4).

CONCLUSIONS

Due to its excellent dielectric and thermal properties of BN–nanotubes, this study has been performed to exhibit physical and chemical properties of interaction between BN–nanotubes and metals.

The hybrid B3LYP density functional theory has been used to characterize the geometry of a BN–nanotube including of two groups of metals (groups I and II of periodic table of elements).

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