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Ab initio study of the structural, mechanical and thermal properties of (B, Al and Ga)-N nanotubes (4,0)

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ABSTRACT

In this work we use density functional theory based on the ultra-soft pseudo-potential to calculate the structural, mechanical and thermal properties of narrow single walled BN, AlN and GaN nanotubes. The electron-electron interactions were expressed within the local density approximation (LDA). We have also obtained the Phonon dispersion and elastic constants of these nanotubes using the density functional perturbation theory. Furthermore the values of Young's modulus, radial breathing mode frequencies and phononic band gaps for BN, AlN and GaN nanotubes (4,0) are reported. Finally it is demonstrated that the behavior of heat capacity of these nanotubes strongly depends on the mass of cations.

Keywords: Density functional theory; Heat capacity; Phonon dispersion; Narrow nano-tubes; QUANTUM ESPRESSO

INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991 [1], the physical, chemical, and electronic properties of these materials have led to a variety of technological uses in many functional nanodevices [2-9]. Also the study of the various nanometres scale tubular structures has attracted many researchers. In the last decades III-V semiconductors and the group III-nitrides in particular have gained extensive attention due to their various potential applications. Therefore the single-walled III-N nanotubes, consist of rolled-up graphene sheets with various chiralities, due to their stability have been the subject of many investigations. Jia et al have investigated the structure and stability of zigzag and armchair boron nitride nanotubes (BNNTs) within the framework of generalized gradient approximated density functional theory [10]. Successful synthesis of pure BNNTs by experimental work has also been reported [11, 12]. Aluminum nitride nanotubes (AlNNTs) with a wide range of different diameters were synthesized either by nitriding impregnated Al powder in a tubular furnace [13] or using the method of highly non equilibrium direct-current arc-plasma-induced melting of aluminum in N-Ar ambient [14]. Carl Hemmingsson et al have also investigated the low temperature growth of GaNNTs by halide vapour phase epitaxy [15]. On the other hand the

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structural and electronic properties of both armchair and zigzag single-walled GaNNTs have been investigated by plane-wave basis DF calculation within the local-density approximation and the SCC-DFTB code [16]. Moreover the stability and electronic properties of single-walled (8,0) and (5,5) InNNTs are predicted by the GAUSSIAN program package [17]. Many efforts have been devoted to investigate the mechanical properties [18-24], optical characterization [25-27] and temperature-dependent transport [28] of III-N nanotubes. Atomistic simulations play an increasingly important role in the elucidation of nanotube properties and development of methods for their fabrication and applications. Computational modeling also provides detailed microscopic information on the physical properties of nanotubes.

The peculiar property of the nanotubes is due small diameter. As is well known the ultrasmall radius SWNTS have many unusual properties. Therefore in the last decades many researches have experimentally and theoretically investigated the properties of ultrathin nanotubes [29-34]. Birykov et al [29] have shown that the narrow nanotubes, with diameter on the order of 1 nm can be a basis for an efficient technique of beam steering at particle accelerators. Zeng et al [30] have studied the transport properties of (2,2) and (3,3) SWNTs by using the DFT associated with noneequilibrium Green function. They have concluded that the electronic properties of small diameter tubes directly relate to large curvature effect. Bezugly et al [31] have systematically studied the electronic band structure and transport properties of a series of zigzag and armchair carbon and boron nanotubes of radii ranging from 0.35 to 16 nm. In Ref.[32] the structural and electronic properties of narrow single walled GaNNTswith diameter from 0.3 to 0.55 nm using DFT are investigated. in this work it is shown that all the armchair and chiral GaNNTs have an indirect gap while zigzag GaNNTs have a direct band gap expect for (4,0) GaNNT. On the other hand Huang and coworkers [33] synthesized BNNTs with average external diameters of sub-10 nm and indicated the ultrafine nanotubes are perfect electrical insulators. Recently in Ref.[34] they have also measured the mechanical properties of BNNTs. Their results demonstrate an obvious transition in mechanics of BNNTs with diameters with the range of 10 nm or less.

In this work we have investigated the structural, mechanical and thermal properties of single walled BN, AlN and GaN zigzag nanotubes (4,0) using the ultra-soft pseudo-potential based on density functional perturbation theory (DFPT). The elastic constants, Young's moduli, radial breathing mode frequencies and phononic band gaps of these nanotubes have been calculated using the obtained phonon dispersion curves. We have also studied the temperature behavior of heat capacity for these nanotubes.

THEORETICAL METHOD

As is well known, in the harmonic approximation, a nanotube consists of a periodic array of ions that oscillate around their equilibrium positions on the surface of any empty tube by thermal energy. The vibration energy of the ions at non-zero temperature has crucial significant effects on mechanical and thermal properties of crystal such as capacity and thermal expansion. The density functional perturbation theory (DFPT) method works under the adiabatic Born-Oppenheimer (BO) approximation. Thus it is assumed that according to any vibrational configuration of the ions, the electronic part of the system remains in the ground state. The phonon frequencies ω are determined by eigenvalues of Hessian of the BO energy *E(r),* scaled by the ion masses [35]:

$$\det\left|\frac{1}{\sqrt{M_I M_J}}\frac{\partial^2 E(R)}{\partial R_I \partial R_J}-\omega^2\right|=0, \qquad (1)$$

where $M_I(M_J)$ denote the mass of the ion at R_I (R_J) position. Therefore, the calculation of vibrational properties of the system needs computing the first and second derivatives of BO energy surface. To do so, the Hellmann-Feynman (HF) theorem would be very helpful,

$$F_I=-\int\frac{\partial V_R(r)}{\partial R_I}n_R(r)dr-\frac{\partial E_N(R)}{\partial R_I}, \qquad (2)$$

$$\frac{\partial^2 E(R)}{\partial R_I \partial R_J}=\int\frac{\partial^2 V_R(r)}{\partial R_I \partial R_J}n_R(r)dr+\int\frac{\partial n_R(R)}{\partial R_J}\frac{\partial V_R(r)}{\partial R_I}dr+\frac{\partial^2 E_N(R)}{\partial R_I \partial R_J}. \qquad (3)$$

To perform the computational procedure, the ground-state electron charge density $n_R(r)$ as well as its linear response to the ionic differential, $\frac{\partial n_{\{R\}}(r)}{\partial R_I}$, must be essentially known. These can be obtained from regular density functional theory (DFT) methods. Therefore, via diagnolization of dynamical matrices (Eq.(1)), it is possible to calculate the phonon dispersion and also the phonon density of states (PHDOS) throughout the Brillouin zone (BZ).

The QUANTUME ESPRESSO code has been applied to calculate the structural, phononic, mechanical and thermodynamic properties of BNNT, AlNNT and GaNNT (4,0). The static energies are computed by means of using the DFT. The phonon frequencies are also calculating by means of using the DFPT. The calculations are carried out under the localized density approximation (LDA). The interactions of the electrons with ion cores are represented by the Vanderbilt-type ultrasoft pseudo-potentials for Ga and N atoms. The Perdew-Wang exchange-correlation functional (PW91) was used for the calculation of electron exchange correlation energy. The wave functions were expanded into plane wave with kinetic energies up to 40 Ry. The summation over the Brillouin zone is carried out with a K-point sampling using Monkhorst-pack grid with parameters of 1×1×12 for BNNT, AlNNT, GaNNT (4,0). All structures have been treated by supercell geometry. The size of the supercell was adjusted to make the interactions between adjacent nanotubes negligible (about 10Å from surface to surface). Optimization of the ionic position, lattice parameters and cell volume were achieved after the relaxation when all forces and stresses become less than 0.25 meV/Å and 0.05 GPa respectively. The Broyden-Flecher-Goldfarb-Shanno (BFGS) algorithm was used to relax the structure of the crystal model. In order to obtain complete phonon dispersion, five dynamical matrices were calculated on a 1×1×8 q-point mesh.

RESULTS AND DISCUSSION

After relaxation it was seen that the cation atoms moved radially toward the tube axes while the nitrogen atoms moved in the opposite direction. In the binary covalant-ionic tublar structures, atoms with more electronegativity tend to move outward and atoms with more electropositivity tends to move inward. Thus the radial geometry of tublar structure is charactrized by two concentric cylindrical tubes. All the cation atoms form the inner cylinder and the all the nitrogen atoms form the outer cylinder. The radial buckling ΔR is defined by:

$$\Delta R=R_N-R_{Cation} \qquad (4)$$

Table 1. The tube radius(R), the periodic length of a unit cell along tube axis (L), buckling separation (ΔR) and bonding length for BNNT, AlNNT and GaNNT (4,0)

NT(4,0)	work	Theory-approximation	R(Å)	L(Å)	ΔR(Å)	III-N bonding length (Å)
BN	present	pwpp-LDA	1.71	4.27	0.153	1.49
	other	pwpp-GGA	1.69[10]	4.23[10]	0.143[10]	1.56 [10]
AlN	present	pwpp-LDA	2.13		0.191	1.82
	other	pp-GGA	-	-	-	1.83[36]
GaN	present	pwpp-LDA	2.152	5.36	0.23	1.90
	other	pp-GGA	2.19[37]	5.37[37]	0.23 [37]	1.90 [38]

where R_N and R_{cation} are the means radii of N and cation atoms cylinders, respectively. In Tab. 1 we summarize the parameters of BN, AlN, GaN nanotubes (4,0) including the tube radius (R), length of a unit cell along tube axis (L), buckling separation(ΔR) and bonding length between III-N atoms. Fig. 1 illustrates the phonon dispersion curves and the corresponding phonon density of states (PHDS) for BNNT, AlNNT and GaNNT (4, 0) obtained by calculating the vibrational frequencies along the tubes' axis (the Z-direction). It can be concluded from this figure that these nanotubes are dynamically stable since all phonon frequencies have positive values through the Brilouin zone. Since the unit cell contains 16 atoms, there are 48 vibrational normal modes. In Fig. 1 two phononic band gaps can be seen for the AlNNT and GaNNT (4,0) while no gap can be seen for the BNNT (4,0). The two gaps for the AlNNT and GaNNT (4,0) may be due to the existence of different kinds of atoms in the Z-direction. The values of these gaps increase by increasing the mass difference of cations and anions (Tab. 2). The lack of band gap in the dispersion curve of BNNT (4,0) is due to small value of the mass difference of cations and anions. So we can regard AlNNT and GaNNT (4,0) as phononic crystal (PC) and opaque barrier [33]. This suggests the potential for designing various phonon optic devices, such as phonon filters, mirrors, resonators, etc. Fig. 2 depicts four acoustic branches at low frequencies near the Γ point: two degenerate TA modes, one LA mode and one twist mode. The twist mode indicates the ionic rotational wave propagation along the tube axis.

According to the close connection between the theory of lattice dynamics and the theory of elasticity the sound velocities can be obtained from the slopes of the acoustic branches of the phonon dispersion relations at Γ point $\left(\mathrm{d}\omega/\mathrm{dk}\right)_{k=0}$. The values of the sound velocities are listed in Tab. 3. As seen from Tab. 3 the LA mode has the highest velocities for (4,0) BNNTs, AlNNTs and GaNNTs. The velocity of the LA, TA and twist modes decreases by increasing the mass of cations. Furthermore the elastic constant along the axis of the nanotube can be calculated by the velocity of LA mode via the relation:

$$V_{LA} = \sqrt{\frac{C_{33}}{\rho}}, \qquad (5)$$

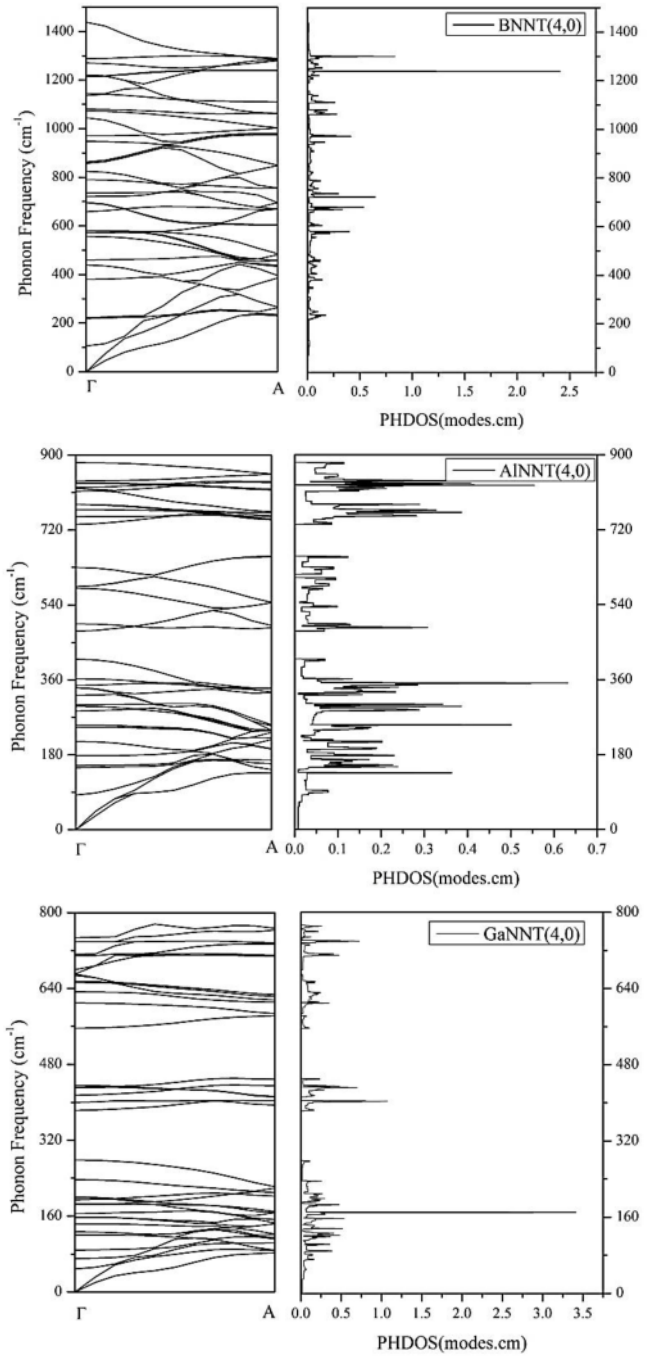

Fig. 1. Phonon dispersion curves and phonon density of states (PHDOS) for BNNT, AlNNT and GaNNT (4,0) along Z direction.

Table 2. The values of phononic band gaps for BNNT, AlNNT and GaNNT (4,0)

NT(4,0)	Phononic band gap (cm^{-1})	Rang of the band gap (cm^{-1})
BN	-	-
AlN	66 and 76	410-476 and 657-733
GaN	101 and 106	275-376 and 443-549

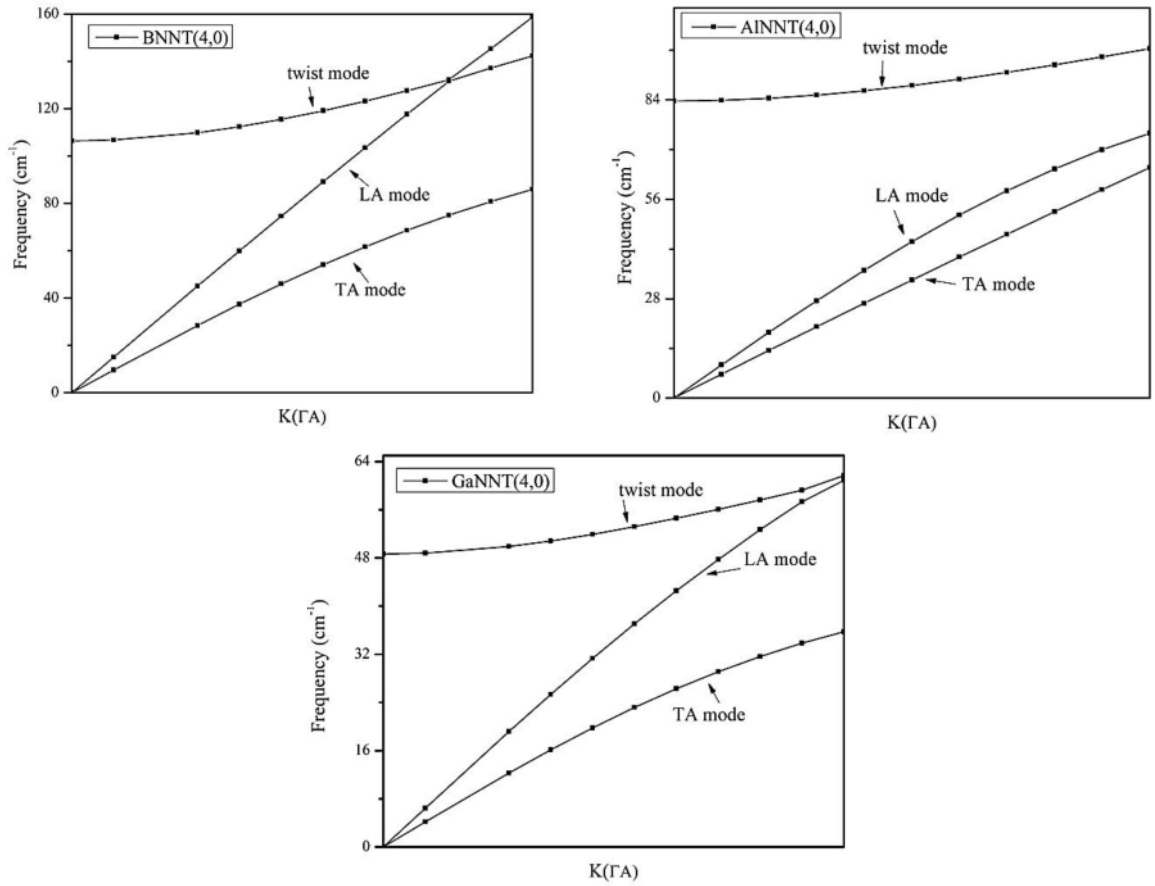

Fig. 2. Acoustic branches around the Γ point.

Table 3. The values of acoustic velocities for BN, AlN and GaN nanotubes (4,0)

NT(4,0)	V_{TA} (km/s)	V_{LA} (km/s)	V_{twist} (km/s)
BN	12.242	19.195	2.677
AlN	10.404	14.427	1.366
GaN	6.595	10.372	1.209

where ρ is the density of the nanotube. In order to calculate the density of the nanotube it is assumed that the BNNT, AlNNT and GaNNT (4,0) are rolled honeycomb-like graphitic sheet with 2.11, 2.50 and 2.62 Å thickness respectively (half of the length of the L parameter for wurtzite phase). Tab. 4 shows that the elastic constant for the BNNT is greater than those for the

Table 4. The values of density, elastic constant and Yong modulus for BNNT, AlNNT and GaNNT (4, 0)

NT(4,0)	$\rho(\frac{kg}{m^3})$	**C_{33}(TPa)**	**Y(TPa)**
BN	3402.910	1.254	1.256
AlN	3149.733	0.655	0.583
GaN	5852.383	0.629	0.497

AlNT and GaNT. Furthermore the Young modulus, Y, is another important mechanical property of nanonubes. As is known the value of Y is defined as:

$$Y = \frac{1}{V_0}\frac{\partial^2 E}{\partial \varepsilon^2}\bigg|_{\varepsilon=0}, \quad (6)$$

where V_0 is the equilibrium volume, E is the total energy, and □ is the subjected strain. Here we calculate Y using the DFT approach by minimizing the total energy with respect to strain along the tube's axis (Murnaghan method). The results are shown in Tab. 4. As it can be concluded from the results of Tab. 1 by reducing the value of bond lengths between the cation and nitrogen atoms in the nanotubes the value of Yong modulus is increased. Therefore the stiffness of the nanotubes will be increased by decreasing the bond lengths between the atoms in nanotubes [40].

Another vibrational characteristic feature of nanotubes is their radial breathing mode (RBM) frequencies (the most important low-frequency Raman active mode). For the RBM, all the atoms move in the radial direction synchronously, which generates an effect similar to "breathing". We note here that RBM has been extensively used in measuring and identifying nanotubes diameter and electronic structures by many researchers. We have listed the values of RBM frequencies in Tab. 5. The dependence of the RBM frequency on the BN and GaN nanotubes diameter, in the elasticity theory, can be respectively expressed as [18]:

$$\omega_{RBM} = \frac{202.16}{d\,(\mathrm{nm})}\,\mathrm{cm}^{-1}, \quad (7)$$

$$\omega_{RBM} = \frac{78.49}{d\,(\mathrm{nm})}\,\mathrm{cm}^{-1}, \quad (8)$$

Our obtained results for RBM values based on ab initio calculation are in good consistent with those obtained from elasticity theory. According to the well-known harmonic mass-spring approximation [34], decreasing the RBM values can be attributed to increase the mass of cations.

After calculating the PHDOS for these single walled nanotubes we have investigated the temperature dependence of their heat capacity according to the following relation:

$$C_v = \int_0^{\nu_{\max}} g(\nu)\left(\frac{\hbar\nu}{k_B T}\right)^2 \frac{e^{\frac{\hbar\nu}{k_B T}}}{(e^{\frac{\hbar\nu}{k_B T}}-1)^2} d\nu \quad (9)$$

where ν is the phonon's frequency, g (ν) is the PHDOS and ν_{max} is the highest frequency of the system which is related to the Debye temperature. The heat capacity directly reflects the details of the excitation spectrum. Therefore we have plotted the heat capacity vs. temperature in Fig. 3. At high temperature, the heat capacity of these binary nanotubes increases by decreasing the mass of cations. In addition the low temperature behavior of heat

Table 5. The values of radial breathing mode (RBM) frequencies for BNNT, AlNNT and GaNNT (4, 0)

NT(4,0)	calculation	BN	AlN	GaN
RBM(cm^{-1})	present	571.45	323.39	185.87
	Eqs.6,7	591[18]	-	182.36

capacity contains information regarding the dimensionality of the system. Nanotubes which are quasi-one dimensional (1D) systems consisting of rolled-up 2D sheets exhibit both 1D and 2D behavior. Fig. 4 shows the heat capacity vs. T and T^2 at low temperature limit. It can be seen from Fig. 4 that at low temperature regime the heat capacity is proportional to T for the BNNT and T^2 for AlNNT and GaNNT (4,0). As it can be seen from Tab. 1 the radius of BNNT (1.71 Å) is smaller than radii of GaNNT (2.15 Å) and AlNNT (2.13 Å). This means that the BNNT bevaves like 1D system while the AlNNT and GaNNT behave seemingly like 2D systems. Therefore we may consider that the behavior of heat capacity of nanotubes is related to the curvature effect at low temperature limit.

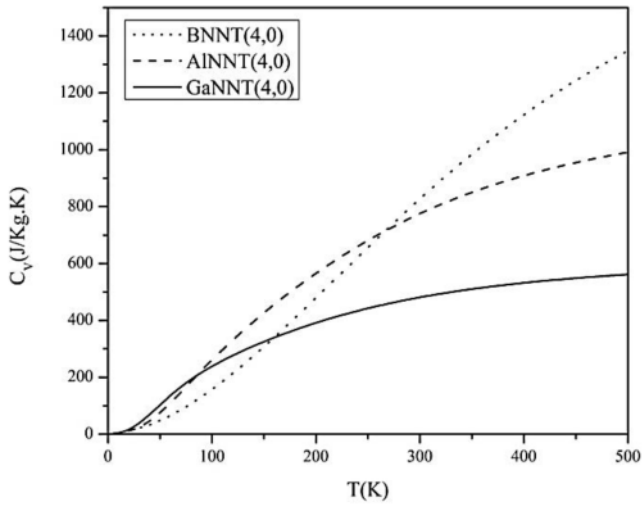

Fig. 3. Temperature dependence of heat capacity for BNNT, AlNNT and GaNNT (4,0).

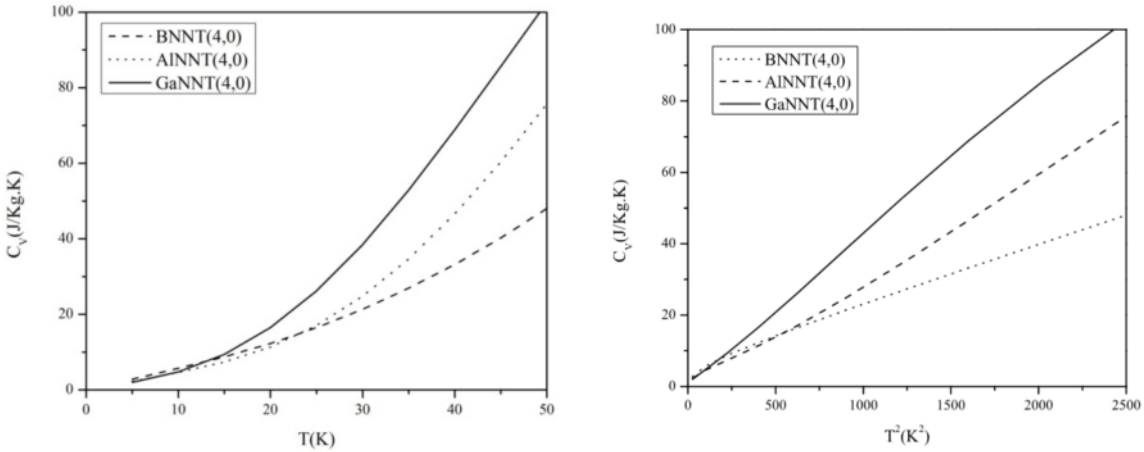

Fig. 4. Heat capacity vs. T and T^2 for BNNT, AlNNT and GaNNT (4,0).

CONCLUSION

The ab initio calculations have been performed to obtain the structural, mechanical and thermal properties of BN, AlN and GaN nanotubes (4,0). We have presented a comparison of the physical properties of these nanotubes. The results

of our calculations for structural properties of BN, AlN and GaN nanotubes (4,0) are in good agreement with the previous theoretical works. Some important phonon quantities such as phononic band gap, RBM frequency and velocity of acoustic modes have also been calculated. The positive phonon dispersion curves demonstrate the dynamical stability of the systems. We have shown that the velocity of the acoustic modes decreases by increasing the mass of cations. It is also shown that the existence of phononic band gap is related to the mass difference of cations and anions. To the best of our knowledge there is no experimental and theoretical data for the elastic constant and young modules for BN, AlN and GaN nanotubes (4,0). Therefore we have calculated these quantities for BN, AlN and GaN nanotubes (4,0). Our calculations show that at low temperature the heat capacity for BNNT is proportional to T while this quantity for AlNNT and GaNNT (4,0) is proportional to T^2. Furthermore it is shown that at high temperature, the heat capacity of these binary nanotubes increases by decreasing the mass of cations.

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