Electronic Supporting Information

Negative/Zero Thermal Expansion in Black Phosphorus Nanotubes

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I. Testing theoretical research method

There are various approaches to perform theoretical study for many kinds of materials, such as molecular dynamics (MD), first principles MD, first principles and so on. BPNT has low symmetry and dimension. As a result, it is almost certainly very anharmonic. For such systems, it is better to use full first principles MD or some type of high order anharmonic lattice dynamics model to reliably predict the thermal expansion. However, there is always a gap between ideal and operability. Huge computing resources and costs caused by such systems using full first principles MD or some type of high order anharmonic lattice dynamics model are often difficult to bear. Therefore, originating from a more comprehensive consideration combined with accuracy and efficiency, we adopt the first principles method to study BPNT system. To test the reliability of first principles method in the case of low-dimensional materials, we have done a testability calculation for thermal expansion of CNTs.

Our calculations for CNTs are performed using the Vienna ab initio simulation package (VASP) within the framework of DFT. The exchange and correlation functional is treated with the generalized gradient approximation (GGA). Plane-wave basis functions with energies up to 500 eV are used. The Brillouin zone integration is approximated with the Monkhorst-Pack method with grids of 1×1×9. All parameters

have been tested for convergence. To study the effects of phonons, we adopt the finite displacement method which involves perturbing the positions of the atoms slightly and calculating the reaction forces. It is necessary to use supercells of the original cells when interatomic interaction in the system is long ranged. In our calculations, the 1×1× 5 supercell with a 0.01 small displacement is used.

Our testability calculations for CNTs have yielded results (see FIG. 1S) that are consistent with other work[1-5]. The NTE behavior in armchair and zigzag CNTs with different diameters can be found.

Returning to our original intention, so it can be obtained that the first principles calculations have certain feasibility for the investigation of nanotubes. This makes it possible for us to carry out the corresponding research for BPNTs.

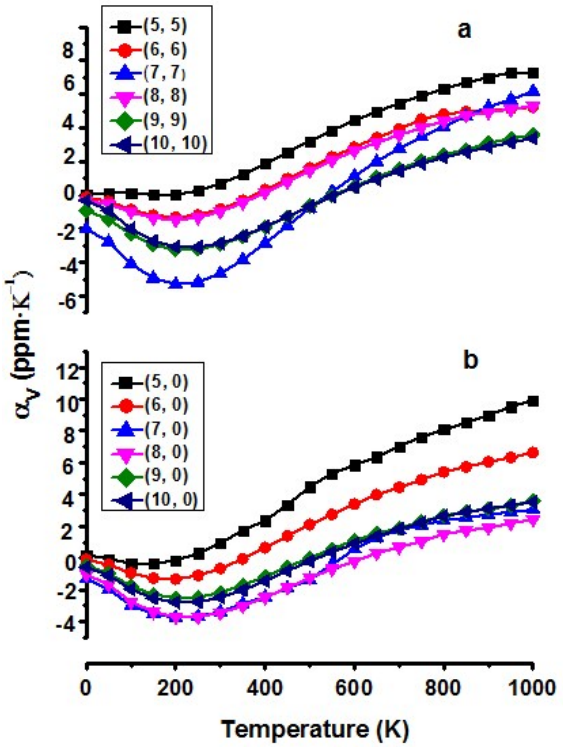

FIG. 1S Temperature dependence of CTEs in (a) armchair (n_1, n_1) CNTs and (b) zigzag (n_1, 0) CNTs ($5 \leq n_1 \leq 10$).

Reference

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II. Related thermodynamic properties in BPNTs

Some related thermodynamic properties such as entropy, heat capacity and free energy in BPNTs are also studied.

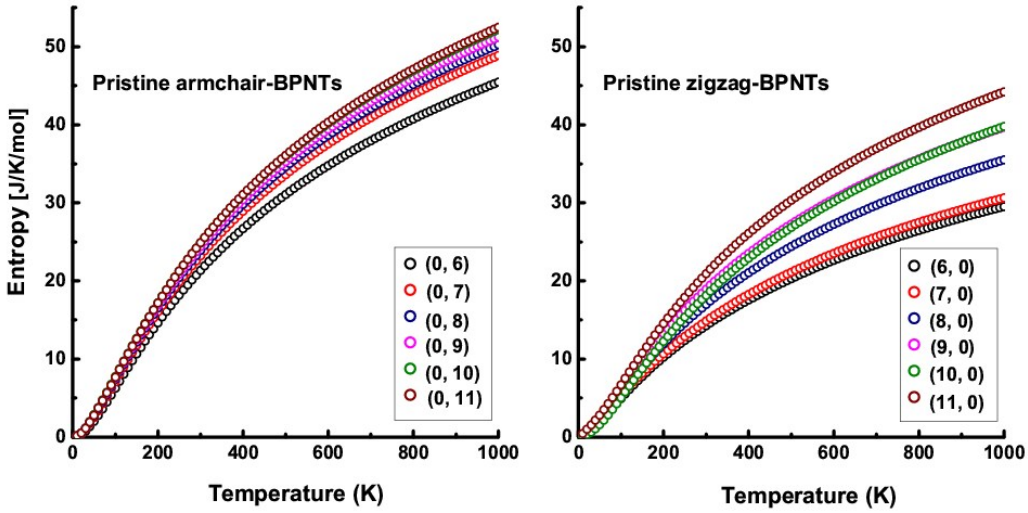

FIG. 2S Temperature dependence of entropy in pristine armchair (0, n_1) and (b) pristine zigzag (n_2, 0) BPNTs ($6 \leq n_1 \leq 11$, $6 \leq n_2 \leq 11$). The entropy in both types of BPNTs increases gradually with increasing diameter.

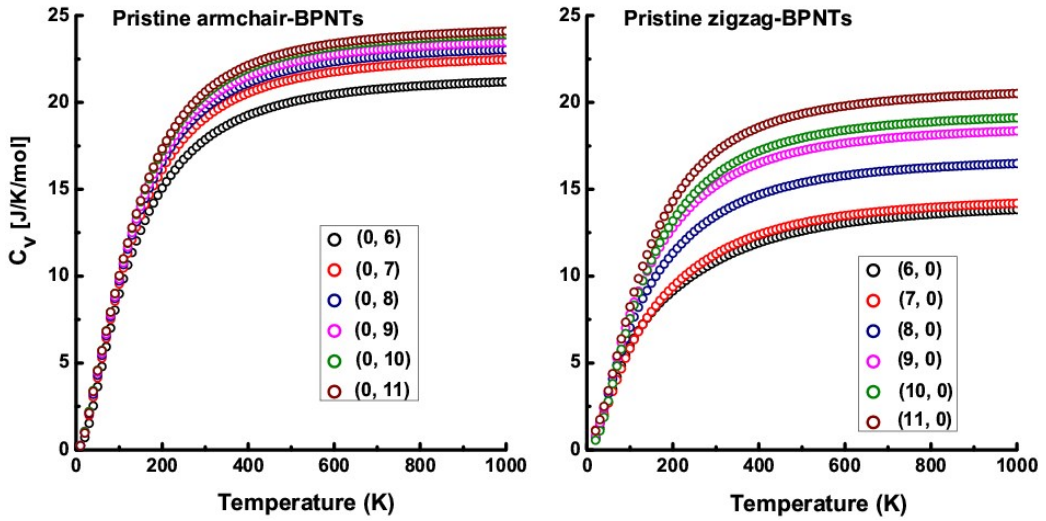

FIG. 3S Temperature dependence of heat capacity at constant volume in pristine armchair (0, n_1) and (b) pristine zigzag (n_2, 0) BPNTs ($6 \leq n_1 \leq 11$, $6 \leq n_2 \leq 11$). The $\boldsymbol{C}_v$ in both types of BPNTs increases gradually with increasing diameter.

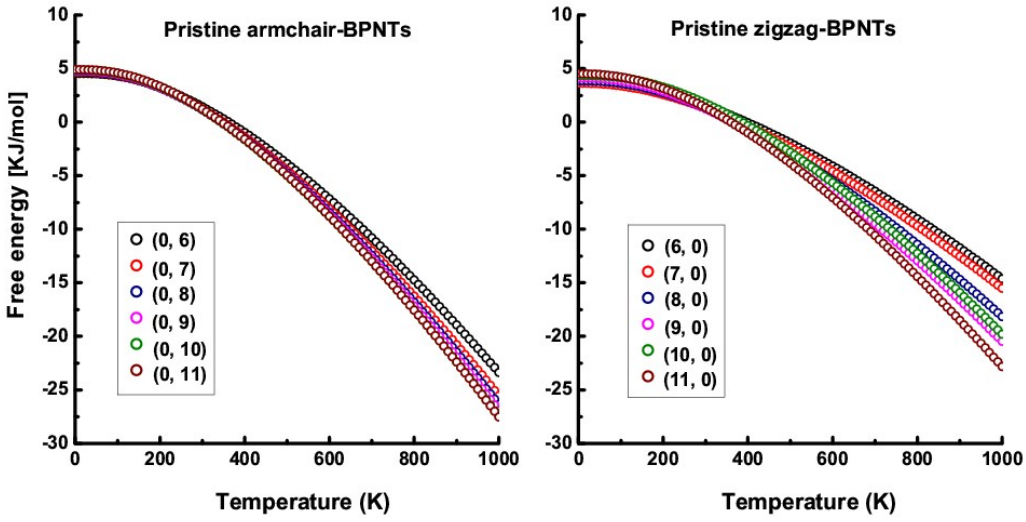

FIG. 4S Temperature dependence of free energy in pristine armchair (0, n_1) and (b) pristine zigzag (n_2, 0) BPNTs ($6 \leq n_1 \leq 11$, $6 \leq n_2 \leq 11$). The free energy in both types of BPNTs decreases gradually with increasing diameter. By comparison, the armchair BPNTs have a faster decline rate of the free energy than zigzag nanotubes.