Prediction of Thermodynamically Stable Compounds of the Sc–N System under High Pressure

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ABSTRACT: Materials under high pressure often exhibit unusual physical and chemical behaviors. We investigated the Sc–N system under high pressure in the range of 0–110 GPa using variable-composition methodology implemented in Universal Structure Predictor: Evolutionary Xtallography (USPEX) in conjunction with Vienna Ab Initio Simulation Package (VASP). The calculation led to prediction of new thermodynamically stable compounds, Sc4N3, Sc8N7, ScN3, and Sc1N5, and also phase transition of ScN5 from triclinic to monoclinic at 104 GPa. These results are important to understand the structure of Sc–N compounds under high pressure and their elastic and electronic properties.

■ INTRODUCTION

Pressure is a fundamental thermodynamic variable that has a capacity to alter the interatomic interactions, electron density distribution, and bonding patterns of materials. These alterations in a material under pressure lead to phase transitions with unusual physical and chemical properties of the material.1 These phases cannot be recovered at ambient condition if the changes of properties are irreversible. Therefore, high-pressure study can be an effective way to discover new functional materials with exciting properties.2–5

The early transition-metal nitrides have significant importance due to their chemical stability and outstanding mechanical properties.6–8 However, scandium nitride (ScN) has attracted significant attention among the early transition-metal nitrides, which is due to its high melting point of 2600 °C, high hardness, extreme corrosive behavior, and electric conductivity.9–12 These remarkable properties categorize scandium nitride as a refractory material and also make it suitable for thermoelectric devices that can be operated at high temperature.13,14

A lot of work has been done on stoichiometric and nonstoichiometric scandium nitrides.15,16 However, most of the work highlights the electronic, optical, and chemical bonding properties in their rock-salt structure.17–19 Many transition metals have a tendency to form nitride compounds under extreme conditions of pressure,20–24 but the question that how many scandium nitride compounds exist is still a mystery. Therefore, we aim in this work to reveal this mystery by exploring crystal structures and all possible stoichiometries of the Sc–N system in the pressure range of 0–110 GPa. Using a state-of-the-art computation technique that has been recently developed, i.e., Universal Structure Predictor: Evolutionary Xtallography (USPEX),25–28 we found several thermodynamically stable compounds with different stoichiometries, Sc4N3, Sc8N7, ScN3, and Sc1N5, under high pressure.

■ RESULTS AND DISCUSSION

To reveal the energetically most favorable structure for the Sc–N compounds under high pressure, we systematically explored the stoichiometric compounds of Sc4N3 in the pressure range of 0–110 GPa. The formation enthalpy for the Sc4N3 compounds was computed relative to dissociation into constituent elements, scandium and nitrogen, by the equation

\[ \Delta H = [H(\text{Sc}_xN_y) - xH(\text{Sc}) - yH(\text{N})]/(x + y) \]

where \( \Delta H \) is the formation enthalpy per atom of a compound and \( H \) is the calculated enthalpy of each constituent element. We constructed a convex hull plot to incorporate all possible decomposition routes of the Sc–N system at pressures of 0, 30, 50, 75, 100, and 110 GPa, as shown in Figure 1. Only the structures located on the convex hull are considered stable structures, and those lying above the convex hull are unstable or metastable structures. At ambient pressure of 0 GPa, the ScN (\text{Fm} \text{3m}, space group 225) compound appears on the convex hull and its calculated lattice parameter \( a = 4.518 \) Å is in good agreement with the experimental values, 4.501 Å and 4.512 Å.30 Hence, this calculation validates the methodology applied to the Sc–N system under zero-pressure condition. Although the Sc4N3, Sc8N7, ScN3, and Sc1N5 compounds are lying above the convex hull at 0 GPa, they become stable at...
higher pressures, as depicted in Figure 1. To reveal the pressure stability of these stoichiometric compounds, we constructed the pressure−composition phase diagram as shown in Figure 2a. Our search reproduced the scandium phases, i.e. ($P6_3/mmc$, space group 194) and ($I4/mmm$, space group 139),31 and also four phases of nitrogen, i.e., ($Pa\bar{3}$, space group 205), ($P2_1/c$, space group 14), ($P4_12_12$, space group 92), and ($I2_13$, space group 199);32 herein, scandium and nitrogen are the basic constituents for the stoichiometric compounds and the appearance of their phases in our search

Figure 1. Convex hull diagram for the Sc−N system under different pressures: (a) 0 GPa; (b) 30 GPa; (c) 50 GPa; (d) 75 GPa; (e) 100 GPa; and (f) 110 GPa. The red solid circles represent the thermodynamically stable compounds, while the open circles represent the unstable structures.
also validates our methodology. The ScN ($Fm\overline{3}m$, space group 225) compound remains thermodynamically stable throughout the considered pressure range. The predicted pressure phase diagram also indicates that the Sc$_8$N$_7$ ($C2/m$, space group 12) compound is stable from 5 to 45 GPa, Sc$_4$N$_3$ ($I4\overline{3}d$, space group 220) compound above 80 GPa, and triclinic ScN$_3$ ($P\overline{1}$, space group 2) above 29 GPa. One of the most interesting predicted structures ScN$_5$ belongs to the family of pentazolate compounds, which have been investigated more closely in recent years than at any time since their first synthesis. CsN$_5$ and NaN$_5$ are newly explored pentazolate compounds; these nitrogen-rich compounds can decompose to dinitrogen N$_2$ with a large energy release. We also explored phase transition of the stoichiometric compound ScN$_5$ at 104 GPa from triclinic to monoclinic, as shown in Figure 2b.

The four new stoichiometric compounds found in our search are shown in Figure 3, and their structural details are summarized in Table 1. The Sc$_4$N$_3$ ($I4\overline{3}d$, space group 220, four formula units) structure has the lattice parameter, $a = 6.225$ Å, at 100 GPa. Inequivalent Sc atoms occupy the Wyckoff position, 16c (0.182, 0.182, 0.182), and the other inequivalent N atoms take the Wyckoff position, 12b (0.875, 0.875, 0.875).

Figure 2. (a) Pressure−composition phase diagram of the Sc−N system in the pressure range of 0−110 GPa; (b) formation enthalpy for ScN$_5$ from the triclinic to monoclinic structures; a phase transition occurs at 104 GPa.

Figure 3. Predicted structures: (a) ScN$_3$ ($P\overline{1}$) at 30 GPa; (b) ScN$_5$ ($P\overline{1}$) at 50 GPa; (c) ScN$_5$ ($Cm$) at 110 GPa; (d) Sc$_8$N$_7$ ($C2/m$) at 30 GPa; and (e) Sc$_4$N$_3$ ($I4\overline{3}d$) at 100 GPa, where the purple sphere represents Sc atom and the gray sphere represents N atom.
Table 1. Structural Details of the Predicted Structures of Sc–N Compounds under Pressure

| phases | pressure (GPa) | space group | lattice parameters $a$, $b$, $c$ (Å) | atom | fractional atomic coordinates | Wyckoff positions |
|--------|---------------|-------------|--------------------------------------|------|-----------------------------|------------------|
| ScN    | 0             | $225$ (Fm$ar{3}$m) | $a = b = c = 4.518$ | Sc (4a) | $x = 0.0$ | 0.0 |
|        | 100           | $220$ (I43d)   | $a = b = c = 6.225$ | N (4e) | $x = 0.182$ | 0.0 |
|        | 30            | $12$ (C2/m)    | $a = b = c = 90.0$ | N (12h) | $x = 0.875$ | 0.25 |
|        | 30            | $2$ (P$ar{6}$) | $a = 13.348$ | N1 (4i) | $x = 0.123$ | 0.0 |
|        | 50            | $2$ (P$ar{6}$) | $b = 3.068$ | N2 (2i) | $x = 0.360$ | 0.0 |
|        | 110           | $8$ (Cm)       | $c = 10.60$ | N3 (2i) | $x = 0.291$ | 0.0 |
|        | 30            | $2$ (P$ar{6}$) | $a = 4.486$ | N1 (2i) | $x = 0.176$ | 0.0 |
|        | 50            | $2$ (P$ar{6}$) | $b = 4.427$ | N2 (2i) | $x = 0.746$ | 0.0 |
|        | 110           | $8$ (Cm)       | $c = 3.034$ | N3 (2i) | $x = 0.598$ | 0.0 |
|        | 30            | $2$ (P$ar{6}$) | $a = 70.349$ | N1 (2i) | $x = 0.364$ | 0.0 |
|        | 50            | $2$ (P$ar{6}$) | $b = 101.130$ | N2 (2i) | $x = 0.737$ | 0.0 |
|        | 110           | $8$ (Cm)       | $c = 103.458$ | N3 (2i) | $x = 0.906$ | 0.0 |
|        | 30            | $2$ (P$ar{6}$) | $a = 4.363$ | N1 (2a) | $x = 0.069$ | 0.0 |
|        | 50            | $2$ (P$ar{6}$) | $b = 4.138$ | N2 (2a) | $x = 0.385$ | 0.0 |
|        | 110           | $8$ (Cm)       | $c = 4.364$ | N3 (2a) | $x = 0.203$ | 0.0 |
|        | 30            | $2$ (P$ar{6}$) | $a = 90.0$ | N1 (4b) | $x = 0.220$ | 0.0 |
|        | 50            | $2$ (P$ar{6}$) | $b = 106.244$ | N2 (4a) | $x = 0.376$ | 0.0 |

0.0, and 0.25). The Sc–N bond length ranges from 2.049 to 2.268 Å. The scandium atom is coordinated with six nitrogen atoms.

The Sc$_2$N$_3$ (C2/m, space group 12, two formula units) stoichiometry has the lattice parameters, $a = 13.348$ Å, $b = 3.068$ Å, $c = 10.60$ Å, $\alpha = 90.0^\circ$, and $\beta = 48.609^\circ$ at 30 GPa. Four inequivalent atoms occupy the Wyckoff positions, Sc1 4i (−0.375, 0.0, 0.313), Sc2 4i (0.126, 0.0, 0.064), Sc3 4i (0.369, 0.0, 0.195), and Sc4 4i (0.123, 0.0, −0.435), and four nitrogen atoms occupy the Wyckoff positions, N1 4i (−0.247, 0.0, 0.370), N2 4i (0.499, 0.0, 0.247), N3 4i (0.251, 0.0, 0.123), and N4 4c (0.0, 0.0, 0.500). The Sc atom is coordinated with six nearby nitrogen atoms, and the bond length of Sc–N is 2.176 Å.

The ScN$_3$ (P1, space group 2, two formula units) has the lattice parameters, $a = 4.486$ Å, $b = 5.057$ Å, $c = 3.034$ Å, $\alpha = 102.192^\circ$, $\beta = 98.35^\circ$, and $\gamma = 99.315^\circ$, at 30 GPa. The scandium atom lies on the Wyckoff position, Sc 2i (−0.208, 0.194, 0.412), and three nitrogen atoms occupy N1 2i (−0.170, −0.324, −0.435), N2 2i (0.360, −0.472, 0.002), and N3 2i (−0.291, −0.124, −0.249). In this structure, N atoms form a chain of six atoms and the shortest distance between them is 1.345 Å. These nitrogen atoms are coordinated with two nearest Sc atoms with a bond length of 2.181 Å.

The ScN$_3$ (P1, space group 2, two formula units) has the lattice parameters, $a = 5.084$ Å, $b = 4.427$ Å, $c = 4.345$ Å, $\alpha = 70.349^\circ$, $\beta = 101.130^\circ$, and $\gamma = 103.458^\circ$, at 50 GPa; the Sc atom occupies the Wyckoff position, Sc 2i (0.187, 0.757, 0.677), while the N atoms occupy the Wyckoff positions, N1 2i (0.746, 0.933, 0.044), N2 2i (0.5987, 0.4306, 0.5854), N3 2i (0.364, 0.170, 0.209), N4 2i (0.737, 0.563, 0.814), and N5 2i (0.906, 0.780, 0.265). However, at 104 GPa, it is transformed to a monoclinic structure with the lattice parameters, $a = 4.138$ Å, $b = 4.138$ Å, $c = 4.364$ Å, $\alpha = 90.0^\circ$, and $\beta = 106.244^\circ$ and the Wyckoff positions, Sc 2a (0.069, 0.0, −0.300), N1 2a (−0.385, 0.0, −0.149), N2 2a (0.203, 0.0, 0.173), N3 4b (0.220, 0.252, 0.349), and N4 2a (−0.376, 0.0, 0.158).

To confirm the dynamic stability of these predicted structures, we recorded the phonon dispersion spectra. It is mandatory for the dynamic stability to have the positive phonon frequencies in the whole Brillouin zone. Any structure having a negative or an imaginary frequency in the Brillouin zone is considered as dynamically unstable. Our recorded phonon spectra in Figure 4 show that there is no imaginary frequency in the whole Brillouin zone, which confirms the dynamic stability of our predicted structures.

The atomic interaction between Sc and N atoms in the Sc–N compounds was revealed by calculating the Bader charges for all predicted stoichiometries at respective pressures. The Bader charges transferred from Sc to N atoms for ScN$_3$, Sc$_2$N$_3$, Sc$_3$N$_3$, and ScN$_2$ are 1.3, 1.6, 1.7, and 1.8, respectively. This also indicates that as the N concentration is increased, the charge transfer from Sc to N also increases. To further explore the bonding nature of compounds, we calculated the electron localization function (ELF), which determines the likelihood of electrons in the nearby space of a crystal. The ELF values generally lie between 0 and 1; the values higher than 0.5 correspond to the covalent bonding, core electrons, and lone

DOI: 10.1021/acsomega.8b01602
ACS Omega 2018, 3, 11477–11485
pairs. The value 0.5 corresponds to the electron gas, while the lower value corresponds to metallic or ionic bonds. As shown in Figure 5, the ELF values are higher between the nearest nitrogen atoms, which shows that the bonding between them is covalent. However, Sc and N formed metallic or ionic bonds because the ELF value is lower between them.

For the electronic properties of the Sc−N system, we calculated the band structure of all of the predicted structures at respective pressures, as shown in Figure 6. The horizontal dashed line in the figure illustrates the Fermi energy level, and bands of all predicted structures are crossing the Fermi level, which shows that our predicted stable structures are metallic in nature. However, we also calculated the band structure of ScN₅.

Figure 4. Phonon dispersion band structure of the predicted structures: (a) ScN₃ (P̅1) at 30 GPa; (b) Sc₂N₇ (C2/m) at 30 GPa; (c) ScN₅ (P̅1) at 50 GPa; (d) Sc₂N₅ (I43d) at 100 GPa; and (e) ScN₅ (Cm) at 110 GPa.
with hybrid function Heyd–Scuseria–Ernzerhof used in density functional theory (DFT), and it opened a narrow band gap 0.24 eV, as shown in Figure 6c.

We also investigated the mechanical stability of the predicted structures because it is the necessary condition for a structure to exist. Elastic constants contain all of the necessary information to understand the mechanical properties and are also helpful for estimating the hardness of a material. We calculated the elastic constants of the predicted structures, which are tabulated in Table 2. These calculated elastic constants satisfy the mechanical stability criteria,35 and the elastic matrix for each compound contains positive eigenvalues,

Figure 5. Mapping of electron localization function (ELF) for the Sc–N system: (a) ScN$_3$ ($P\bar{1}$) at 30 GPa; (b) Sc$_2$N$_6$ ($P\bar{1}$) at 50 GPa; (c) Sc$_3$N$_3$ ($I\bar{4}3d$) at 50 GPa; (d) ScN$_5$ ($Cm$) at 110 GPa; and (e) Sc$_8$N$_7$ ($C2/m$) at 30 GPa, where the purple sphere represents Sc atom and the gray sphere represents N atom.

Figure 6. Electronic band structure of the predicted structures: (a) ScN$_3$ at 30 GPa; (b) Sc$_8$N$_7$ at 30 GPa; (c) ScN$_5$ at 50 GPa; and (d) Sc$_4$N$_3$ at 100 GPa.
Table 2. Calculated Elastic Stiffness Constants $C_{ij}$, Bulk Modulus $B$, Shear Modulus $G$, Young’s Modulus $E$, Poisson’s Ratio $\nu$, and Vickers Hardness $H_v$ of the Sc–N System

| $C_{ij}$ constants | ScN cubic | Sc$_3$N$_7$, monoclinic | Sc$_3$N$_7$, triclinic | ScN$_3$, triclinic | ScN$_5$, monoclinic | ScN$_5$, cubic |
|--------------------|-----------|-------------------------|-----------------------|-------------------|------------------|-----------------|
| $C_{11}$           | 385.81    | 549.92                  | 426.18                | 599.99            | 772.45           | 788.63          |
| $C_{12}$           | 498.73    | 443.61                  | 457.08                | 821.69            |                  |                 |
| $C_{13}$           | 464.91    | 563.28                  | 414.57                | 861.50            |                  |                 |
| $C_{44}$           | 163.74    | 162.13                  | 138.72                | 215.40            | 426.77           | 165.11          |
| $C_{15}$           | 212.21    | 192.74                  | 129.65                | 329.39            |                  |                 |
| $C_{16}$           | 159.67    | 240.07                  | 237.03                | 311.42            |                  |                 |
| $C_{12}$           | 104.70    | 110.58                  | 224.26                | 329.12            |                  | 221.93          |
| $C_{13}$           | 124.52    | 137.47                  | 266.51                | 373.19            |                  |                 |
| $C_{14}$           | 0.2770    | 32.47                   | 42.87                 | 109.77            |                  |                 |
| $C_{15}$           | 0.2782    | 32.94                   | 82.25                 |                  |                  |                 |
| $C_{16}$           | 166.43    | 168.97                  | 152.66                | 343.03            |                  |                 |
| $C_{14}$           | −0.071    | −16.75                  | −53.96                | −75.21            |                  |                 |
| $C_{15}$           | −0.019    | −8.31                   | −27.54                | 0.74              |                  |                 |
| $C_{16}$           | 29.81     | 31.63                   |                      |                  |                  |                 |
| $C_{13}$           | 55.13     | 10.41                   |                      |                  |                  |                 |
| $C_{14}$           | 0.002     | 8.91                    | 34.17                 | 145.83            |                  |                 |
| $C_{15}$           | 0.95      | −21.99                  |                      |                  |                  |                 |
| $C_{16}$           |           |                        |                      |                  |                  |                 |

| $B$ (GPa)          | 198.38    | 257.32                  | 262.56                | 307.28            | 484.49           | 410.94          |
| $G$ (GPa)          | 154.46    | 178.44                  | 154.53                | 171.4             | 269.94           | 205.33          |
| $E$ (GPa)          | 367.89    | 434.81                  | 387.57                | 433.58            | 682.98           | 528.04          |
| $\nu$              | 0.191     | 0.218                   | 0.254                 | 0.265             | 0.265            | 0.286           |
| $H_v$ (GPa)        | 25        | 24                      | 17.5                  | 17.4              | 23.6             | 17.0            |

which further proves the elastic stability of the considered structures. Bulk modulus and shear modulus depict the material resistance to volumetric changes and shape deformation; materials with high bulk modulus are considered strong in resisting uniform compression, while materials with high shear modulus can have high hardness because shear modulus is related to hardness. The calculated values of $B$, $G$, and $H_v$ are tabulated in Table 2, which shows that the bulk modulus increases as the nitrogen content increases in the compound. For the ScN cubic structure, our calculated elastic constants $C_{11}$, $C_{12}$, and $C_{44}$ and bulk modulus of 198.38 GPa are in good agreement with the literature value, 198 GPa, which further proves the elastic stability of the considered structures. Bulk modulus and shear modulus depict the material resistance to volumetric changes and shape deformation; materials with high bulk modulus are considered strong in resisting uniform compression, while materials with high shear modulus can have high hardness because shear modulus is related to hardness. The calculated values of $B$, $G$, and $H_v$ are tabulated in Table 2, which shows that the bulk modulus increases as the nitrogen content increases in the compound. For the ScN cubic structure, our calculated elastic constants $C_{11}$, $C_{12}$, and $C_{44}$ and bulk modulus of 198.38 GPa are in good agreement with the literature value, 198 GPa, which supports our calculation for other structures as well because there is no published data on these compounds to the best of our knowledge. The estimated hardnesses of ScN, Sc$_3$N$_7$, and ScN$_5$ compounds are 25, 24, and 23.6 GPa, respectively, while those of ScN$_3$, ScN$_5$, and ScN$_3$ are 17.5, 17.4, and 17.0 GPa, respectively. The bulk modulus-to-shear modulus ratio, $k = G/B$, indicates the ductility and brittleness of a material; the critical value of $k$ is about 1.75. The materials having $k$-values greater than 1.75 are ductile and those having lower values are brittle. The calculated Pugh ratios for ScN, Sc$_3$N$_7$, and ScN$_3$ are 1.28, 1.44, and 1.69, respectively, indicating that these compounds are brittle. However, the Pugh ratios for ScN$_3$ and ScN$_3$ are 1.79 and 2.0, respectively, indicating that they are ductile. The ductility and brittleness of a material can also be differentiated by Poisson’s ratio, whose value greater than 0.26 indicates better ductile materials. Poisson’s ratio $\nu$ also gives insights into the characteristics of bonding forces: for covalent materials, the value is 0.1, while for ionic materials, it is 0.25. For a central force solid, the value is between 0.25 and 0.5.

Table 2 shows our calculated values of $\nu$ and indicates that for ScN$_3$ and Sc$_3$N$_7$, the interatomic force is central while for ScN, Sc$_3$N$_7$, and ScN$_3$, it has ionic bonding characteristics.

**CONCLUSIONS**

In summary, we systematically investigated the Sc–N system in the pressure range of 0–110 GPa using variable-composition methodology implemented in USPEX in conjunction with VASP. The calculation enables us to find new thermodynamically stable compounds, Sc$_3$N$_3$, Sc$_3$N$_7$, Sc$_4$N$_3$, and ScN$_5$. We also explored the phase transition of ScN$_3$ from triclinic to monoclinic at 104 GPa. Our results are also important for understanding the structures, electronic properties, and elastic properties of Sc–N compounds under high pressures.

**COMPUTATIONAL DETAILS**

To discover all potential Sc$_n$N$_2$ structures under high pressure for the Sc–N system, an extensive search for stable compounds was performed using the evolutionary algorithm and variable-composition strategy implemented in USPEX code in conjunction with Vienna Ab Initio Simulation Package (VASP). The variable-composition evolutionary search was carried out at pressures of 0, 30, 50, 75, 100, and 110 GPa by keeping 8–16 atoms in a primitive cell to find stable compositions. Then, we performed a fixed-composition search of each of these stable compositions with different formula units. The first-generation structures were produced randomly, and the number of structures in this generation was kept large. The resultant structures were obtained by applying different operators in the following percentages: heredity, 40%; lattice
mutation, 20%; and atom transmutation, 20%, while 20% randomly produced structures were also added in each generation. The USPEX calculation efficiency is found to increase by applying these key parameters.

Total energy calculations were executed in the density functional theory (DFT) framework within the Perdew–Burke–Ernzerhof parametrization of generalized gradient approximation, as implemented in VASP code. The projector-augmented wave method described the interaction between the ions and the electrons with a cutoff energy of 520 eV. The 3d4s5 (cutoff radius, 2.5 au) and 2s2p3 (cutoff radius, 1.5 au) were treated as valence states in the Sc and N atoms, respectively. A uniform Γ-centered Monkhorst–Pack grid with a higher resolution of \( 2\pi \times 0.03 \ \text{Å}^{-1} \) was used to sample the Brillouin zone, which also confirmed that the total energies were \( \leq 10^{-3} \text{eV/atom} \). Moreover, all forces on atoms were converged to \( \leq 10^{-3} \text{eV/Å} \) and the total stress tensor deviated from the target pressure by \( \leq 10^{-2} \text{GPa} \). The phonon dispersion curve was calculated to determine the dynamical stability of the predicted structures using the finite displacement methodology, as implemented in the PHONOPY code. The charge transferred was calculated using Bader’s quantum theory. All structures were visualized and plotted using VESTA. The elastic stiffness constants were calculated using the strain–stress methodology. We used the ELATE code to obtain the bulk modulus \( B \), shear modulus \( G \), Young’s modulus \( E \), and Poisson’s ratio. There are several models to calculate the theoretical Vickers hardness, but Chen’s model is considered more accurate. We used Chen’s model to estimate the theoretical Vickers hardness \( H_v \) by the relation, \( H_v = 2(k^2G)^{1/3} - 3 \), where \( k = G/B \) is the Pugh ratio.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the National Natural Science Foundation of China (No. 11574289), “111” Project of the Education Ministry of China (No. B07033), and Special Program for Applied Research on Supercomputing of the NSFC-Guangdong Joint Fund (2nd phase) under Grant No. U1501501. The authors also thank Dr H. M. Li and acknowledge the supercomputing center of USTC for the support of parallel computing.

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