Supporting Information for

$Na_3Y_3(BO_3)_4$: a new noncentrosymmetric borate with an open-framework structure

Faxian Shan,[a,b] Lei Kang,[a,b] Guochun Zhang,*[,a] Jiyong Yao,[a] Zheshuai Lin,[a] Mingjun Xia,[a] Xinyuan Zhang,[a,b] Ying Fu[a,b] and Yicheng Wu[a]

[a]Beijing Center for Crystal R&D, Key Lab of Functional Crystals and Laser Technology of Chinese Academy of Sciences, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China.

[b]University of Chinese Academy of Sciences, Beijing 100049, PR China.

Corresponding author: Guochun Zhang; gczhang@mail.ipc.ac.cn.

Tel: 86-10-82543726; Fax: 86-10-82543726.

Experimental Details

Single Crystal Growth

Single crystals were grown in the Na_2CO_3–B_2O_3–NaF flux system by spontaneous crystallization method. A mixture of Na_2CO_3 (Beijing Beihua Fine Chemical Reagent Co., Ltd., 98%), Y_2O_3 (Changchun Haipurui Rare Earth Material Co., Ltd., 99.99%), B_2O_3 (Sinopharm Chemical Reagent Co., Ltd., 98%), and NaF (Xilong Chemical Reagent Co., Ltd., 98%) in molar ratio of 9:2:14:10 was ground in an agate mortar and then transferred into a platinum crucible. The sample was heated up to 1050 ºC and maintained for 16 h to ensure that it was melted thoroughly and mixed homogeneously. Then the solution was cooled at a rate of 1.5 ºC/h to 750 ºC, and followed by natural cooling to room temperature. The product consisted of colorless and transparent crystals in six-sided columns.

Single Crystal X-ray Diffraction

Single crystal X-ray diffraction data for $Na_3Y_3(BO_3)_4$ was collected at 153 K on a Rigaku AFC10 single-crystal diffractometer from 3.81−31.53° with a graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å) and Saturn CCD detector. A colorless transparent crystal with dimension of 0.215 × 0.08 × 0.065 mm^3 was selected for structure determination. Crystalclear program was run to record the intensity data and perform cell refinement and data reduction.[1] The structure was solved with Shelxtl-97 by the direct method and refined by full-matrix least-squares techniques with anisotropic thermal parameters.[2]

Crystal data for $Na_3Y_3(BO_3)_4$, M = 570.94 g/mol, hexagonal, a = 10.1136(14) Å, c = 6.7485(13) Å, V = 597.79(16) $Å^3$, T = 153 K, Z = 2, space group $P6_3mc$ (No.186), 5803 reflections measured. The final R_1 values were 0.0481 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1097 ($I > 2\sigma(I)$). The final R_1 values were 0.0596 (all data). The final $wR(F^2)$ values were 0.1143 (all data). Goodness-of-fit on F^2 = 0.906.

Calculation of Space Utilization

The space utilization (atomic packing factor[3]) equals to the total volume of atoms in a unit cell divided by the cell volume. For comparison purposes, $CsLiB_6O_{10}$,[4] $Bi_{0.9}Y_{3.09}Sr_3B_4O_{15}$,[5] $RbBe_2BO_3F_2$,[6] $CsBe_2BO_3F_2$,[6] $KBe_2BO_3F_2$,[7] BiB_3O_6,[8] CsB_3O_5,[9] $NaCoB_6O_{11}$,[10] LiB_3O_5,[11] BPO_4,[12] and $YAl_3(BO_3)_4$[13] with relatively low space

utilization were chosen. The two known borates[14,15] $Na_3Y(BO_3)_2$ and $Na_2Y_2O(BO_3)_2$ in the Na_2O–Y_2O_3–B_2O_3 system were also investigated.

The space utilizations (atomic packing factors) of $Na_3Y_3(BO_3)_4$ and several typical borate are displayed in Figure S2. It is clear that $Na_3Y_3(BO_3)_4$ exhibits the lowest space utilization, which results from its close elemental constituents and the discernible tunnel structure (one hexagonal tunnel with a diameter up to 5.92 Å per unit cell).

First-principles Calculations

To verify the structural stability, phonon spectra calculations on $Na_3Y_3(BO_3)_4$ was performed. The positive eigenvalues for all phonon modes in Fig. S3 is the most important evidence for the structural stability. This method on structural stability was also adopted by Yao[16] and Sheng[17].

To investigate the NLO property of $Na_3Y_3(BO_3)_4$, the first-principles calculations on its electronic band structure and optical properties, including UV absorption edge, SHG coefficients and birefringence, were performed. The ion-electron interactions were modeled by the norm-conserving pseudopotentials for all constituent elements.[18] In this model, Na $2s^22p^63s^1$, Y $4d^15s^2$, B $2s^22p^1$, and O $2s^22p^4$ electrons were treated as the valence electrons, respectively. The ultra-fine kinetic energy cutoff of 770 eV and Monkhorst-Pack *k*-point meshes[19] spanning less than 0.04/Å^3 in the Brillouin zone were chosen in order to ensure the sufficient accuracy of the plane-wave pseudopotential method[20] implemented in the CASTEP package[21]. According to the previous studies by Lin et al,[22] the PBE0 method was employed to calculate the UV absorption edge,[23] while the scissors-corrected local density approximation (LDA) method[24-26] was adopted to obtain the SHG coefficients[27] and birefringence.

Table S1. Crystal data and structure refinements for $Na_3Y_3(BO_3)_4$

	$Na_3Y_3(BO_3)_4$
fw	570.94
a (Å)	10.1136(14)
c (Å)	6.7485(13)
γ (°)	120.00(0)
V (Å^3)	597.79(16)
Space group	$P6_3mc$
Z	2
T (K)	153(2)
λ (Å)	0.71073
ρ_c (g/cm^3)	3.172
μ (cm^{-1})	14.609
$R(F)^a$	0.0481
$R_W(F_o^2)^b$	0.1143
Flack parameter	0.04(3)

$^aR(F) = \sum \big| \, |F_o| - |F_c| \, \big| / \sum |F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.

$^bR_w(F_o^2) = \{\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4\}^{1/2}$ for all data. $w^{-1} = \sigma^2(F_o^2) + (zP)^2$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; $z = 0.01$.

Table S2. Selected bond lengths (Å) and bond angles (°) for $Na_3Y_3(BO_3)_4$

Na–O1	2.494 (8)	Y1–O2	2.266 (5)
Na–O1	2.496 (5)	Y1–O3	2.247 (5)
Na–O2	2.517 (11)	Y1–O3	2.247 (7)
Na–O3	2.884 (8)	Y1–O3×2	2.605 (6)
Na–O3	2.885 (8)	B1–O1	1.387 (3)
Na–O3	2.413 (10)	B1–O1	1.387 (6)
Na–O3	2.414 (10)	B1–O1	1.387 (7)
Y1–O1	2.428 (6)	B2–O2	1.448 (16)
Y1–O1	2.292 (4)	B2–O3	1.353 (16)
Y1–O2	2.266 (3)	B2–O3	1.354 (16)
O1–B1–O1×3	119.85 (11)	O3–B2–O2×2	113.6 (7)
		O3–B2–O3	132.7 (14)

Fig. S1 Coordination environment of Y and Na atoms. (The blue, green, and red balls represent Y, Na, and O atoms, respectively.)

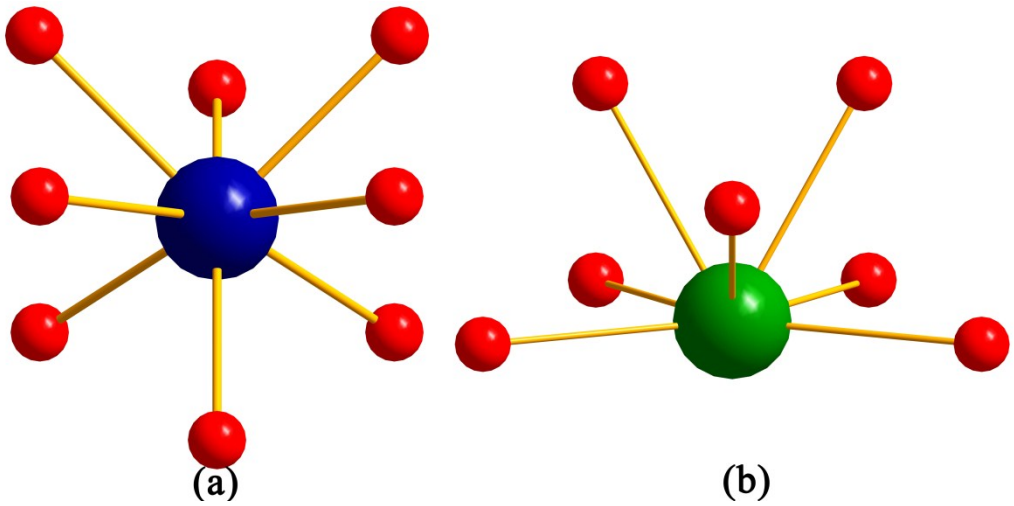


Fig. S2 The space utilizations of $Na_3Y_3(BO_3)_4$ and several typical borates.

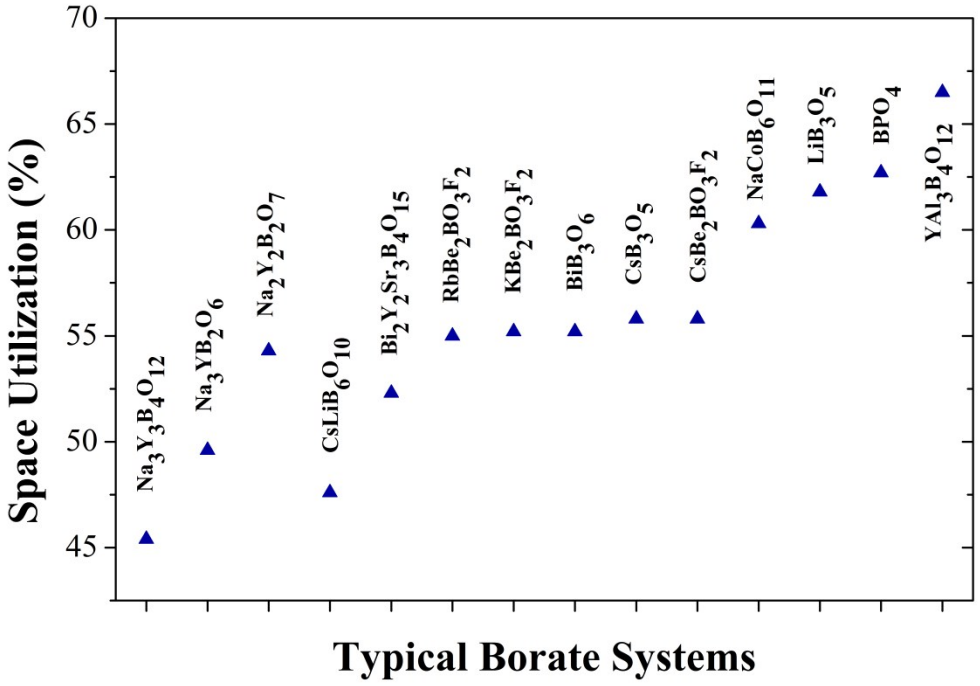


Fig. S3 The phonon vibration spectrum of $Na_3Y_3(BO_3)_4$.

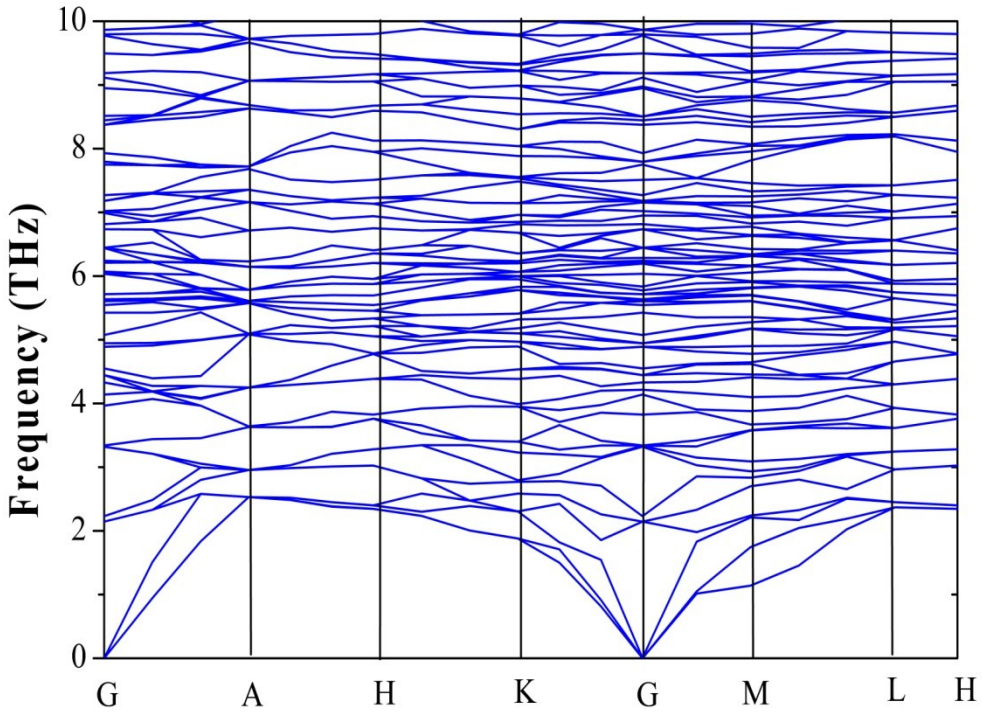


Fig. S4 The calculated dispersion curve of refractive index.

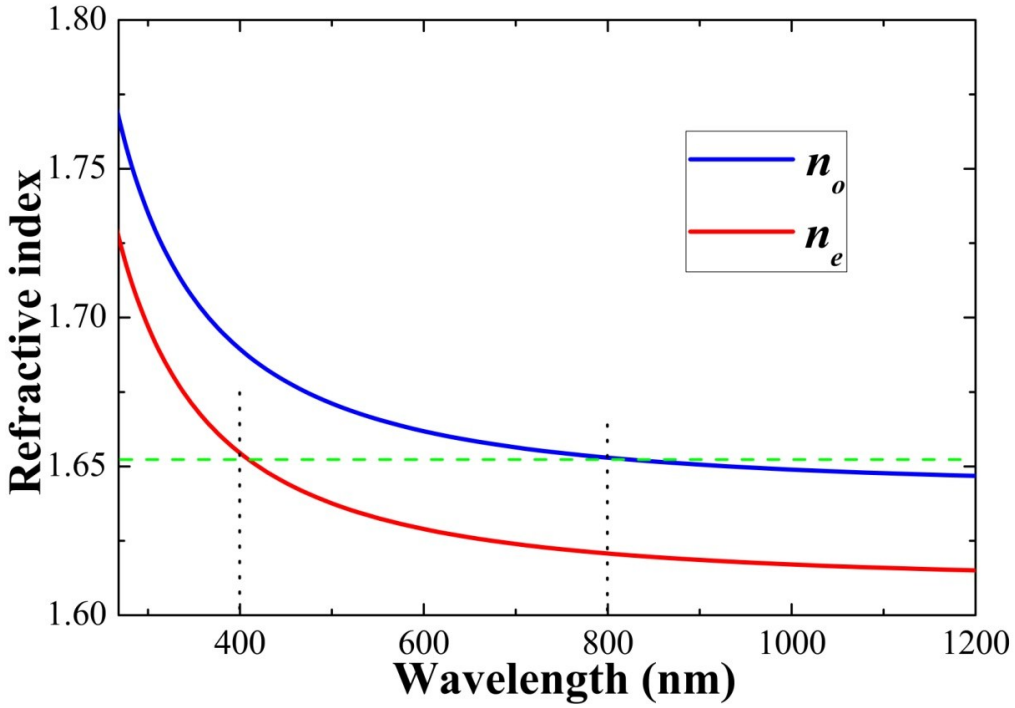


Fig. S5 The partial density of states (PDOS) of $Na_3Y_3(BO_3)_4$ crystal.

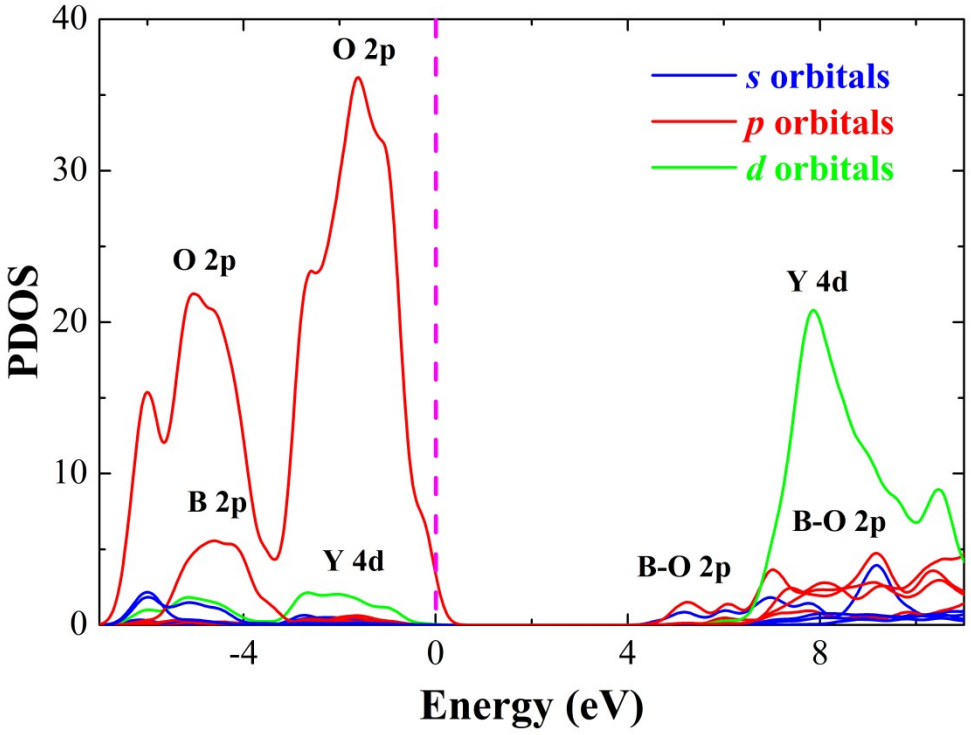
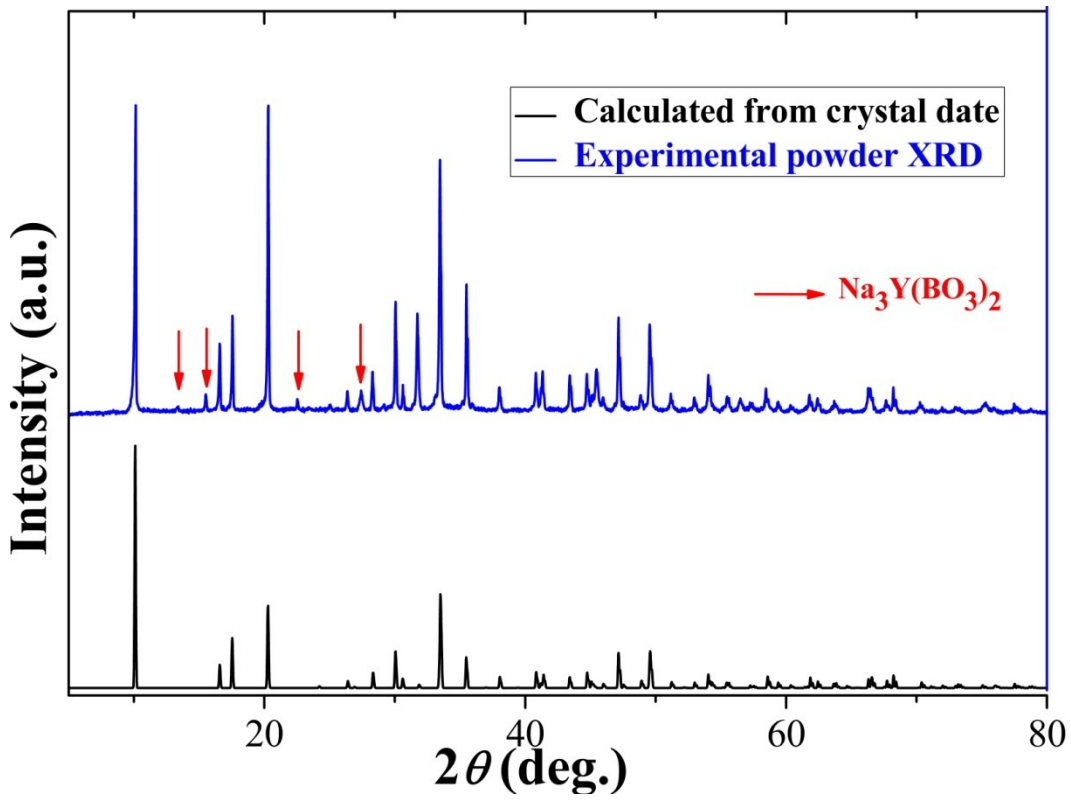


Table S3. The calculated values of SHG coefficients of $Na_3Y_3(BO_3)_4$.

$Na_3Y_3(BO_3)_4$	Calculated SHG coefficients (pm/V)
Total	$d_{31} = d_{32} = 0.45$; $d_{33} = -1.28$
Na^+	$d_{31} = d_{32} = 0.01$; $d_{33} = 0.01$
$(BO_3)^{3-}$	$d_{31} = d_{32} = 0.36$; $d_{33} = -1.09$
$(YO_8)^{13-}$	$d_{31} = d_{32} = 0.27$; $d_{33} = -0.72$

Fig. S6 The experimental and calculated X-ray diffraction patterns of $Na_3Y_3(BO_3)_4$. (The blue curve is the experimental pattern of synthesized samples, and the black one is the calculated pattern.)



Reference

[1] CrystalClear, Rigaku Inc., Tokyo, 2008.

[2] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2008**, 64**, 112–122.

[3] J. W. D. Callister and D. G. Rethwisch, *Materials science and engineering: an introduction*, John Wiley & Sons Inc., New Jersey, 2010.

[4] J. M. Tu and D. A. Keszler, *Mater. Res. Bull.*, 1995, **30**, 209-215.

[5] J. H. Gao and S. Li, *Inorg. Chem.*, 2012, **51**, 420-424.

[6] C. D. McMillen, J. Hu, D. VanDerveer and J. W. Kolis, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2009, **65**, 445-449.

[7] J. Q. Yu, L. J. Liu, S. F. Jin, H. T. Zhou, X. L. He, C. L. Zhang, W. N. Zhou, X. Y. Wang, X. L. Chen and C. T. Chen, *J. Solid State Chem.*, 2011, **184**, 2790-2793.

[8] W. D. Stein, A. Cousson, P. Becker, L. Bohaty and M. *Z.* Braden, *Kristallogr.*, 2007**, 222**, 680-689.

[9] J. Krogh-Moe, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.*, 1974, **30**, 1178-1180.

[10] J. L. C. Rowsell, N. J. Taylor and L. F. Nazar, *J. Am. Chem. Soc*., 2002, **124**, 6522-6523.

[11] Y. F. Shepelev, R. S. Bubnova, S. K. Filatov, N. A. Sennova and N. A. Pilneva, *J. Solid State Chem.*, 2005, **178**, 2987-2997.

[12] S. N. Achary and A. K. Tyagi, *J. Solid State Chem.*, 2004, **177**, 3918-3926.

[13] G. Meszaros, E. Svab, E. Beregi, A. Watterich and M. Toth, *Phys. B (Amsterdam, Neth.)*., 2000, **276**, 310-311.

[14] Y. Zhang, X. L. Chen, J. K. Liang and T. Xu, *J. Alloys Compd.*, 2002, **333**, 72-75.

[15] Y. Zhang and Y. D. Li, *J. Alloys Compd.*, 2004, **370**, 99-103.

[16] Y. Yao, J. S. Tse, J. Sun, D. D. Klug, R. Martonak and T. Iitaka, *Phys. Rev. Lett.*, 2009, **102**, 229601.

[17] X. L. Sheng, Q. B. Yan, F. Ye, Q. R. Zheng and G. Su, *Phys. Rev. Lett.*, 2011, **106**, 155703.

[18] D. R. Hamann, M. Schluter and C. Chiang, *Phys. Rev. Lett*., 1979, **43**, 1494-1497.

[19] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1976, **13**, 5188.

[20] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias and J. D. Joannopoulos, *Rev. Mod. Phys*., 1992**, 64**, 1045-1097.

[21] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson and M. C. Payne, *Z. Kristallogr.*, 2005**, 220**, 567-570.

[22] Z. S. Lin, L. Kang, T. Zheng, R. He, H. Huang and C. T. Chen, *Comput. Mater. Sci.*, 2012, **60**, 99-104.

[23] C. Adamo and V. Barone, *Chem. Phys. Lett*., 1998, **298**, 113-119.

[24] D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett*., 1980, **45**, 566-569.

[25] C. S. Wang and B. M. Klein, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1981, **24**, 3393-3416.

[26] R. W. Godby, M. Schluter and L. J. Sham, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 10159-10175.

[27] J. Lin, M. H. Lee, Z. P. Liu, C. T. Chen and C. J. Pickard, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **60**, 13380-13389.