Supporting information

A new ultraviolet transparent hydra-cyanurate $K_2(C_3N_3O_3H)$ with strong optical anisotropy from delocalized π-bonds

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Experimental methods

Synthesis of single crystal $K_2(C_3N_3O_3H)$

The crystals of $K_2(C_3N_3O_3H)$, was successfully synthesized by slow evaporation method in aqueous solution.

$$H_3C_3N_3O_3 + 2KOH \rightarrow K_2(C_3N_3O_3H) + 2H_2O$$

potassium hydroxide and cyanuric acid were stirred and heat in 3:1 molar ratio in aqueous solution. After those a catalytic amount of acidic acid should be added slowly until a transparent solution was formed, then heating the solution up to its boiling point until water was evaporated and cools down. Colorless crystals with prismatic shape were obtained from resulting white precipitate and washed with alcohol. This method has advantage of excellent quality, short time and high production efficiency which can produce enough crystal in a short time.

X-ray diffraction

Single-crystal X-ray diffraction measurement was carried out on a Rigaku AFC10 diffractometer equipped with a graphite-monochromated (Mo K_a k = 0.71073 Å) radiation at 293 K. The collection of intensity data was carried out with Crystalclear. Crystal structures were solved by direct methods and refined in the SHELXTL system.[1] Final least-squares refinement includes anisotropic displacement parameters for all atoms. The structure was verified using the ADDSYM algorithm from the program PLATON, and no higher symmetry was found. An automated Bruker D8 ADVANCE X-ray diffractometer equipped with a diffracted monochromator set for CuK_α (λ = 1.5418 Å) radiation was used to measure the powder XRD patterns. The measurements were performed in the angular range of 2θ =5–70° with a scan step width of 0.02° and a fixed counting time of 0.05 s per step.

Thermal Analysis

By equipped with the nitrogen flow at a rate of about 20 mL/min, LabsysTM TG-DTA16 (SETARAM) thermal analyzer was implied to investigate the thermal stability of $K_2(C_3N_3O_3H)$. after thoroughly ground, 5mg of polycrystalline powder were placed in a silica tube (5 mm o.d. × 3 mm i.d.) and subsequently sealed under a high vacuum. The tube was heated from room temperature to 973 K and then cooled to room temperature with the heating/cooling rate both at 30 K/ min. The thermogravimetric analysis is experimented by NETZSCH STA 2500 thermal analyzer. 3 mg grinded sample was heated from 303 K to 1473K with heating rate at 10K/min.

Transmission spectrum

The transmittance spectrum from UV to near-IR range (0.2–2.5 μm) was recorded on a Shimadzu SolidSpec-3700 DUV spectrophotometer by pure phase grind samples. In addition, the reflectance spectra were converted to absorbance spectra through the Kubelka–Munk function.[2]

IR and Raman spectroscopy

Fourier transform infrared spectra (FTIR) of three compounds in the range of 400-4000 cm^{-1} were recorded on an Excalibur 3100 FT-IR spectrometer (Varian, Inc.). Room temperature Raman spectrum of the title compound was measured using an InVia-Reflex Raman spectrometer (Renishaw, Inc.) with exciting wavelength at 632.8 nm.

Theoretical Calculations

The first-principles calculations on $K_2(C_3N_3O_3H)$ were performed in the framework of density functional theory[3] by the pseudo-potential methods implemented in the CASTEP package.[4] The total energy calculations including full structural optimizations were carried with the generalized gradient approximation (GGA) method with PBE functional.[5] The optimized norm-conserving pseudopotentials[6] were used to simulate ion-electron interactions for all constituent elements, including K $4s^1$, H $1s^1$, B $2s^22p^1$, C $2s^22p^2$, N $2s^22p^3$, O $2s^22p^4$. A kinetic energy cutoff of 700 eV was chosen with Monkhorst-Pack *k*-point meshes spanning less than 0.04/Å^3 in the Brillouin zone.[7] The choice of these computational parameters is good enough to ensure the accuracy of the present purpose. Based on the calculated band structure, the imaginary part of the dielectric function was calculated and the real part of the dielectric function was determined using the Kramers–Kronig transformation, and then the refractive indices n and the birefringence Δn were obtained. This calculation method has been applied in many inorganic optoelectronic materials successfully.[8] Meanwhile, the linear response method was employed to obtain the phonon dispersion and vibrational modes of crystal.[9] The ultrafine dispersion separation of 0.01/Å^3 and high cutoff energy of 1000 eV is adopted to make sure the good convergence.

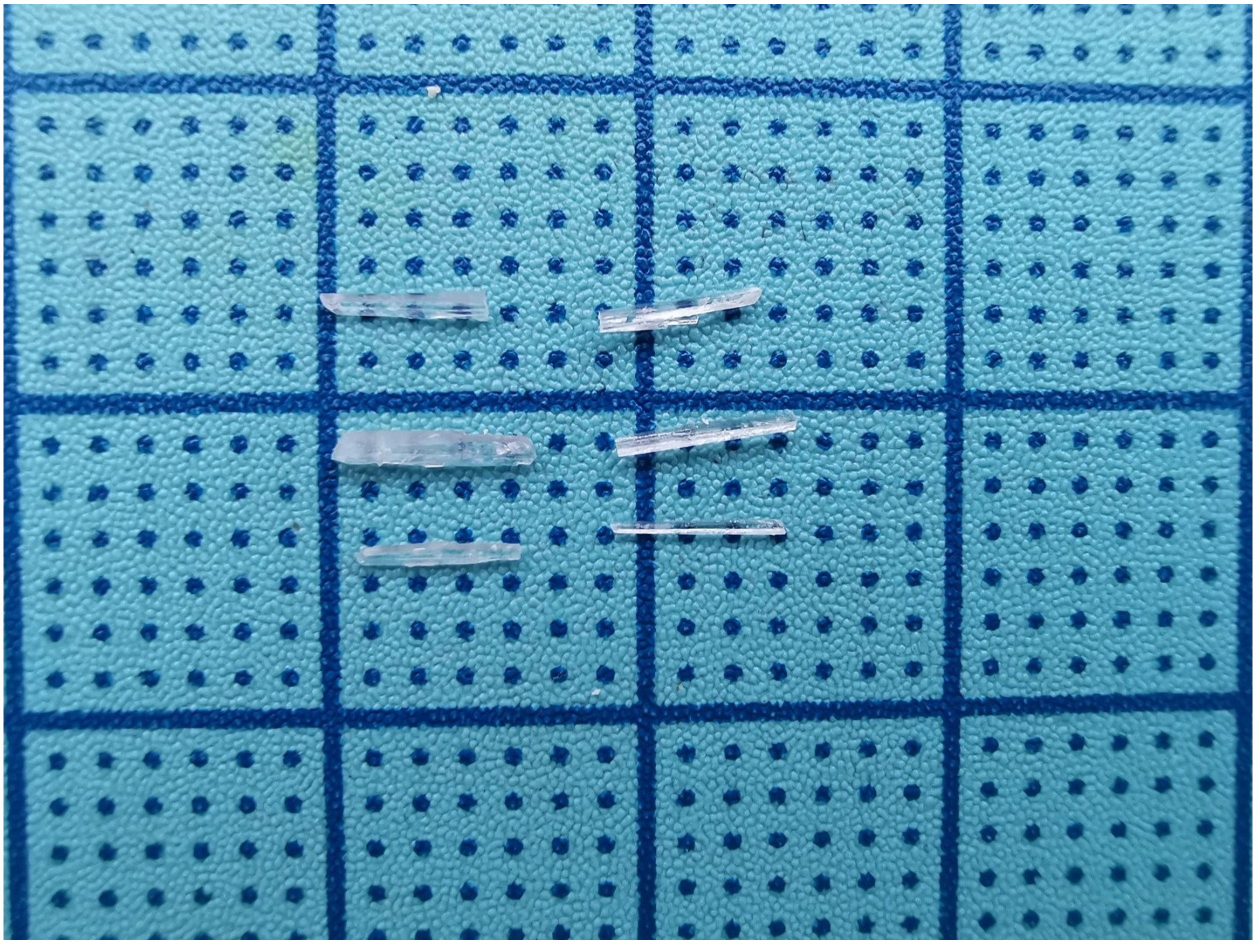


Figure S1. Photograph of the $K_2(C_3N_3O_3H)$ crystal.

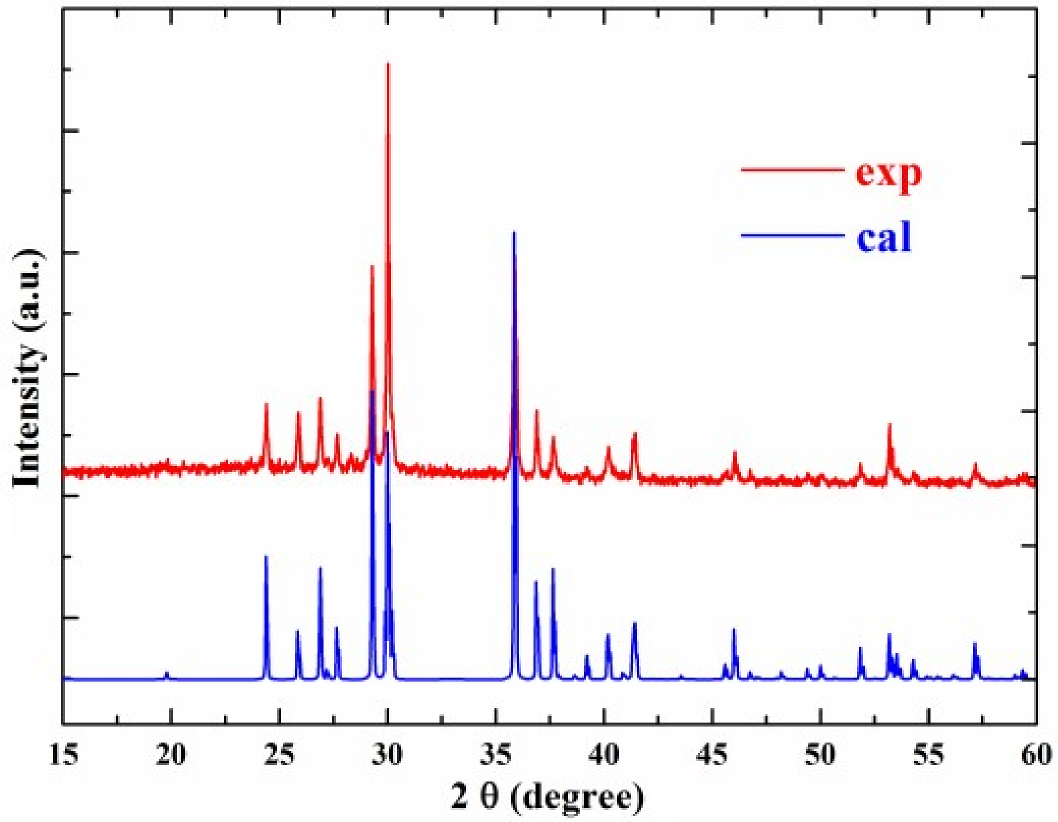


Figure S2. Powder X-ray diffraction patterns of $K_2(C_3N_3O_3H)$.

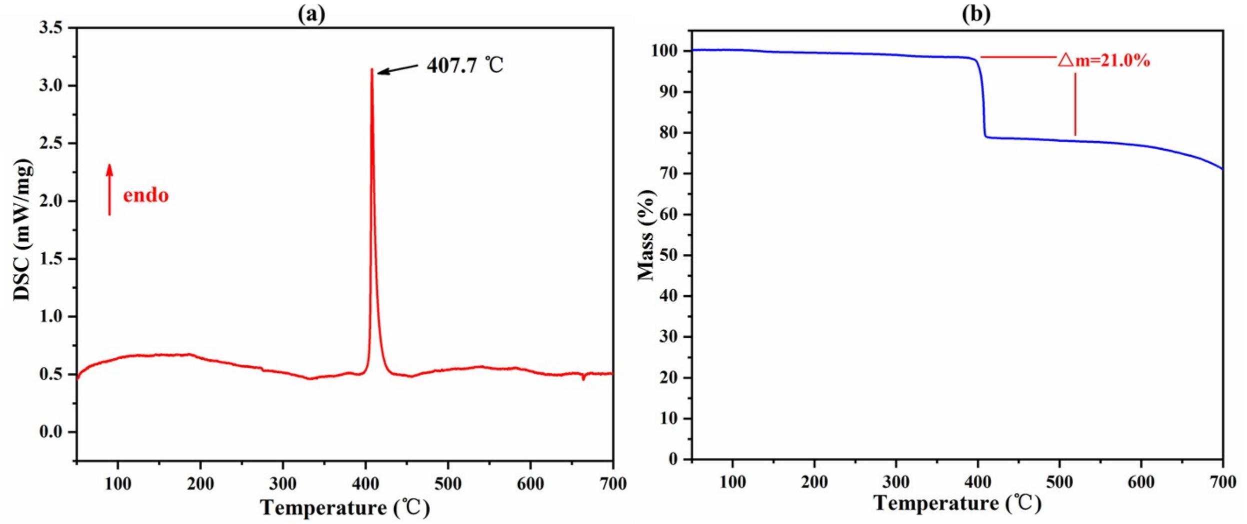
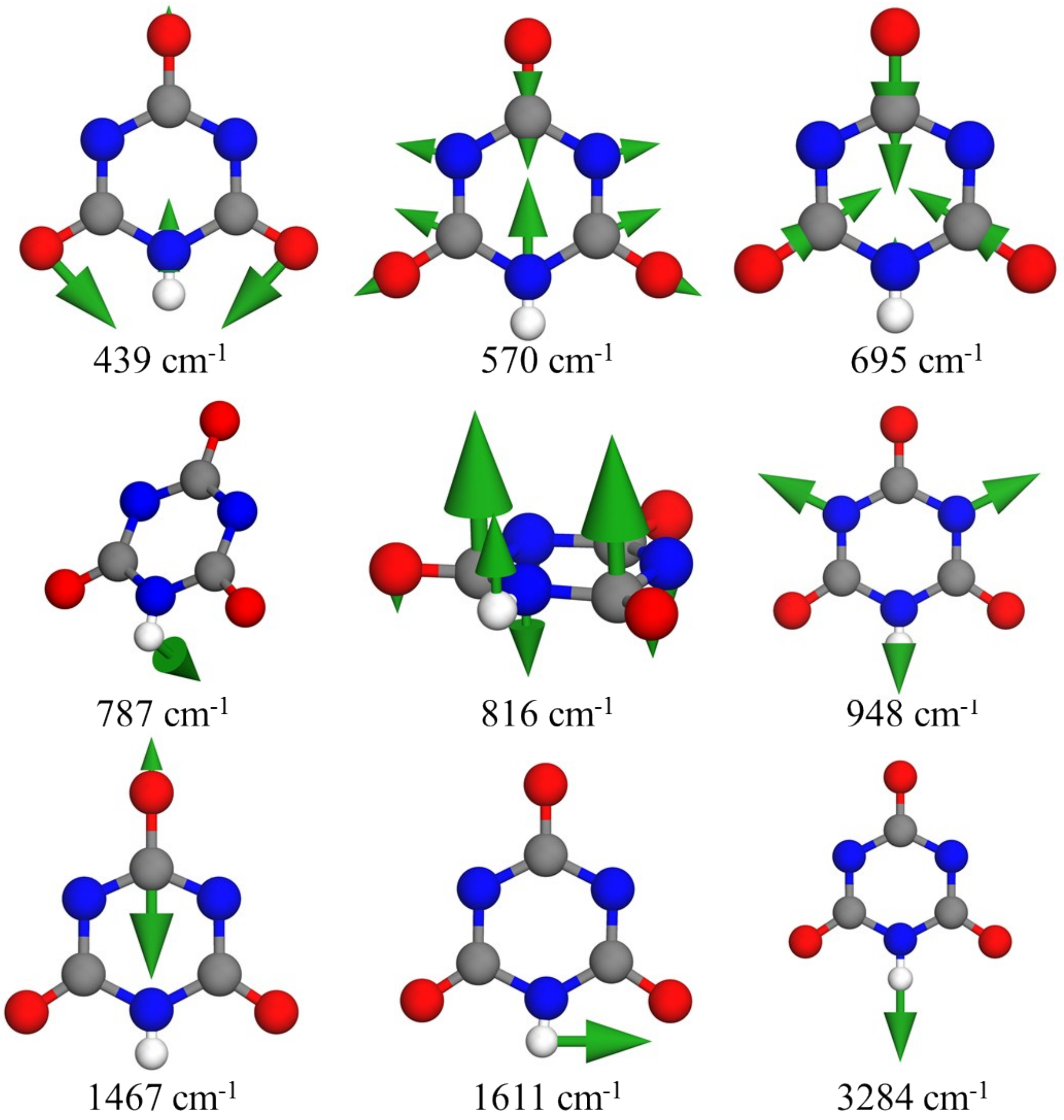


Figure S3. Thermal analysis of $K_2(C_3N_3O_3H)$: (a) shows DSC curves of $K_2(C_3N_3O_3H)$, There is only one sharp endothermic peak at 407.7 °C when it was heated; (b) displays TG curves of $K_2(C_3N_3O_3H)$, the main changing of mass loss occurred at 407 °C, the proposed reaction is: $3K_2(C_3N_3O_3H) \rightarrow 2K_3(C_3N_3O_3) + 3HCNO$.


439 cm^{-1} 570 cm^{-1} 695 cm^{-1}

787 cm^{-1} 816 cm^{-1} 948 cm^{-1}

1467 cm^{-1} 1611 cm^{-1} 3284 cm^{-1}

Figure S4. The simulated vibrational mode of $K_2(C_3N_3O_3H)$ based on phonon calculations.

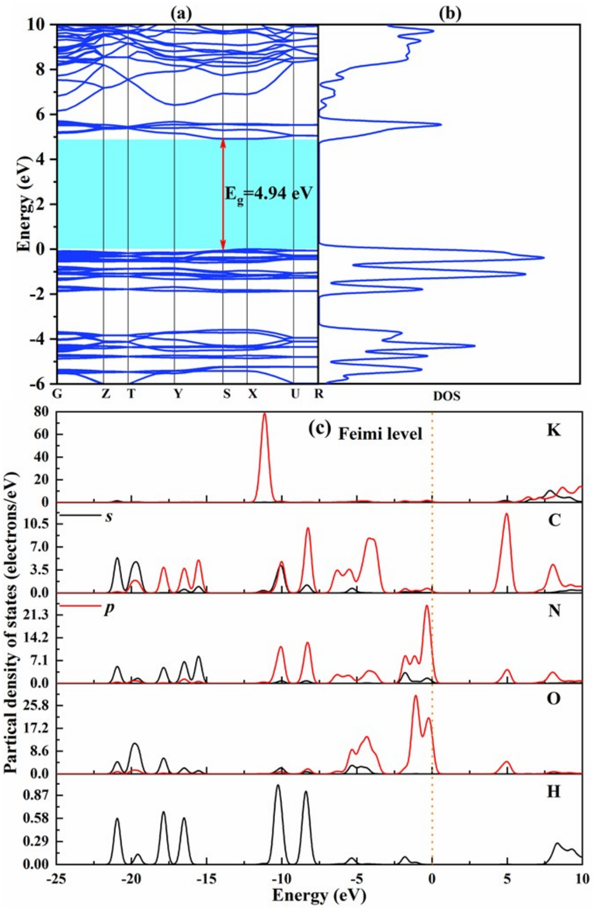


Figure S5. (a) Scissor corrected band structure and (b) total, (c) partial of density of states of K($C_3N_3O_3H$).

Table S1. Crystallographic data for $K_2(C_3N_3O_3H)$.

Empirical formula	$K_2(C_3N_3O_3H)$
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	Cmcm
a (Å)	13.0970(6)
b (Å)	6.6265(3)
c (Å)	6.8836(3)
alpha (°)	90
beta (°)	90
gamma (°)	90
Volume ($Å^3$)	597.41(5)
Z	4
Density (g/cm^3)	2.282
μ (mm^{-1})	1.534
F(000)	408.0
Theta range for data collection (deg)	3.111 to 28.967
Limiting indices	$-17 \leq h \leq 17$, $-9 \leq k \leq 8$, $-8 \leq l \leq 9$
Data / restraints / parameters	439/0/39
GOF on F^2	1.214
Final R indices [I>2sigma(I)]	$R_1 = 0.0254$, $wR_2 = 0.0649$
R indices (all data)	$R_1 = 0.0266$, $wR_2 = 0.0659$
Largest diff. peak and hole ($eÅ^{-3}$)	0.45/-0.29

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for $K_2(C_3N_3O_3H)$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	Wyckoff site	U_{eq}
O_2	0.67241(7)	0.35103(18)	2.5	g	0.0205(3)
O_1	0.5	0.9448(3)	0.2500	c	0.0299(5)
N_2	0.5	0.3579(3)	0.25	c	0.0182(4)
N_1	0.59302(9)	0.65875(18)	0.25	g	0.0178(3)
C_2	0.59252(10)	0.4564(2)	0.25	g	0.0141(3)
C_1	0.5	0.7518(3)	0.25	c	0.0172(4)
K_1	0.82159(2)	0.5	0.5	e	0.0225(2)

Table S3. Selected bond lengths (Å) and angles (degree) for $K_2(C_3N_3O_3H)$.

$K_1 - O_2^{9}$	2.7845(8)	C_2-N_2-C_2^{8}	123.41(17)
$K_1 - O_2^{9}$	2.7845(8)	C_2-N_1-C_1	116.57(13)
$K_1 - O_2^{10}$	2.8946(10)	O_2-C_2-N_2	118.00(13)
$K_1 - O_2^{3}$	2.8946(10)	O_2-C_2-N_1	123.43(13)
$K_1 - O_1^{7}$	2.9249(3)	N_1-C_2-N_2	118.57(13)
$K_1 - O_1^{11}$	2.9249(3)	O_1-C_1-N_1	116.85(9)
$K_1 - O_2^{9}$	2.7845(8)	O_1-C_1-N_1^{8}	116.85(9)
$K_1 - O_2^{10}$	2.8946(10)	N_1^{8}-C_1-N_1	126.30(18)
C_1 –O_1	1.279(3)		
C_1 - N_1^{8}	1.3654(16)		
C_2 –O_2	1.2577(17)		
C_2 –N_2	1.3762(16)		
C_2^{8}–N_2	1.3762(16)		
C_2–N_1	1.3412(17)		

^{1}+X,+Y,1/2-Z; ^{2}3/2-X,1/2-Y,-1/2+Z; ^{3}3/2-X,1/2-Y,1-Z; ^{4}3/2-X,3/2-Y,1-Z; ^{5}-1/2+X,1/2+Y,1/2-Z; ^{6}-1/2+X,1/2+Y,+Z; ^{7}3/2-X,3/2-Y,-1/2+Z; ^{8}1-X,+Y,1/2-Z; ^{9}+X,1-Y,1/2+Z; ^{10}3/2-X,1/2+Y,1/2-Z; ^{11}1/2+X,-1/2+Y,+Z; ^{12}3/2-X,-1/2+Y,1/2-Z; ^{13}+X,+Y,3/2-Z

References

1. G. M. Sheldrick, *Acta Crystallogr. Sec. A*, 2008, **64**, 112-122.
2. S. K. Loyalka and C. A. Riggs, *Appl. Spectrosc.* , 1995, **49**, 1107-1110.
3. W. Kohn, *Rev. Mod. Phys.* , 1999, **71**, 1253-1266.
4. 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.
5. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* , 1996, **77**, 3865-3868.
6. M. Rappe, K. M. Rabe, E. Kaxiras and J. D. Joannopoulos, *Phys. Rev. B*, 1990, **41**, 1227-1230.
7. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188-5192.
8. S. Lin, X. X. Jiang, L. Kang, P. F. Gong, S. Y. Luo and M. H. Lee, *J. Phys. D-Appl. Phys*, 2014, **47**, 253001.
9. Baroni, S. de Gironcoli, A. Dal Corso and P. Giannozzi, *Rev. Mod. Phys.* , 2001, **73**, 515-562.