Supporting information

Linear Triatomic $[ZnBi_2]^{4-}$ in K_4ZnBi_2

Qian Qin, Liujiang Zhou, Yi Wang, Ruili Sang, Li Xu*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002.

1.1   Synthesis

All the chemicals were obtained from commercial sources and was handled in N_2 atmosphere using an N_2-filled glovebox. K was purified by liquating, Zn powder (99.99%, ChemPur) and Bi granules (99.99%, ChemPur) were used as received.

K_4ZnBi_2 are obtained unexpected by reactions of the K, Zn and Bi elements at the rate of 3:1:2 in welded niobium containers that were sealed in an evacuated fused silica jacket (20mm i.d.) under high vacuum (ca. 10^{-3} Pa). The assembly were heated at 700℃ for 2 days and then cooled to room temperature, with isothermal dwelling times of 48 hours at 450℃. A cooling rate of 5℃ h^{-1} was used for the steps 700℃ to 450℃ and 450℃ to room temperature.

The pure powder of K_4ZnBi_2 are synthesized by reactions of the stoichiometric proportions of the elements in welded niobium containers that were sealed in an evacuated fused silica jacket (20mm i.d.) under high vacuum (ca. 10^{-3} Pa). And then heated to 700℃ in 2 hours. The sample was stayed at 700℃ for 2 days, then quickly putted into cold water.

1.2 The data collection

The intensity data were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated MoKα radiation (λ= 0.71073 Å) at room temperature.   All absorption corrections were performed using multiscan. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with the SHELXTL-97 program package.

1.3 X-ray Powder Diffraction

The sample was assessed for phase purity using powder X-ray diffraction. As the sample of K_4ZnBi_2 is sensitive to air and moisture, it was protected by the Magic Tape when it was tested. XRD pattern were collected on a Rigaku DMAX 2500 powder diffractometer with ultra 18 Kw Cu Kα radiation. The dates are treated by jade 6.0.
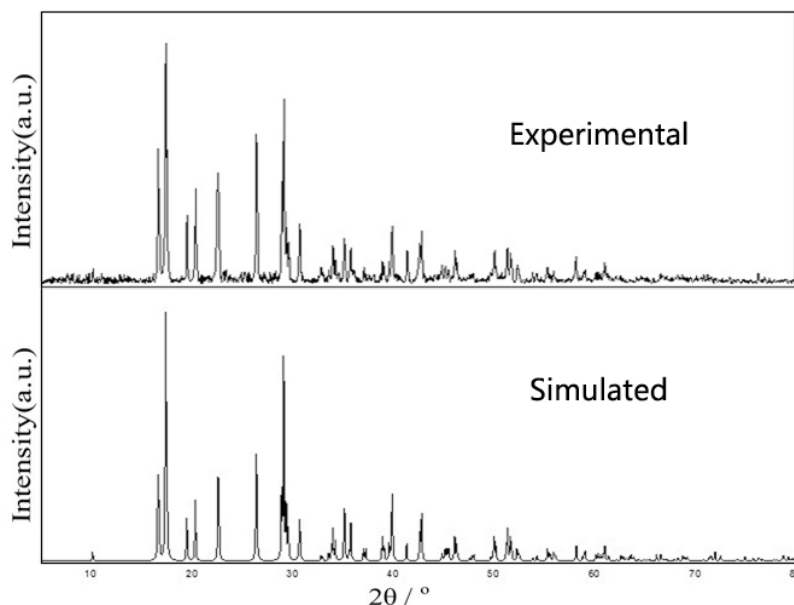
Fig. S1   Experimental and simulated X-ray powder diffraction patterns of K_4ZnBi_2.

1.4 Computational descriptions

First principle studies of band structures and density of states (DOS) were performed by using the projector augmented wave (PAW) method,[1] as implemented in the Vienna ab initio simulation package (VASP)[2]. The Perdew-Burke-Ernzerhof (PBE)[3] functional of the generalized gradient approximations (GGA)[4] was employed as the exchange-correlation function. The valence atomic configurations were $3s^23p^64s^1$, $3d^{10}4s^2$, $5d^{10}6s^26p^3$, for K, Zn, and Bi, respectively. The plane-wave cutoff energy of 277 eV and the threshold of 10^{-5} eV were set for the self-consistent-field convergence of the total electronic energy. For DOS calculations, we used a 9 × 9 × 3 Monkhorst-Pack k-point grid within the Brillouin zone.

1.   G. Kresse and D. Joubert, *Physical Review B* 1999, **59**, 1758.

2.   G. Kresse and J. Furthmüller, *Physical Review B* 1996, **54**, 11169.

3.   J. P. Perdew, K. Burke and M. Ernzerhof, *Phys Rev Lett* 1996, **77**, 3865.

4.   J. P. Perdew and Y. Wang, *Physical Review B* 1992, **45**, 13244.

2. Crystal structure determination

Space group determination

Mean │E×E-1│=0.566 [expected 0.968 centrosymmetry and 0.736 non-centrosymmetry]
Systematic absence exceptions:

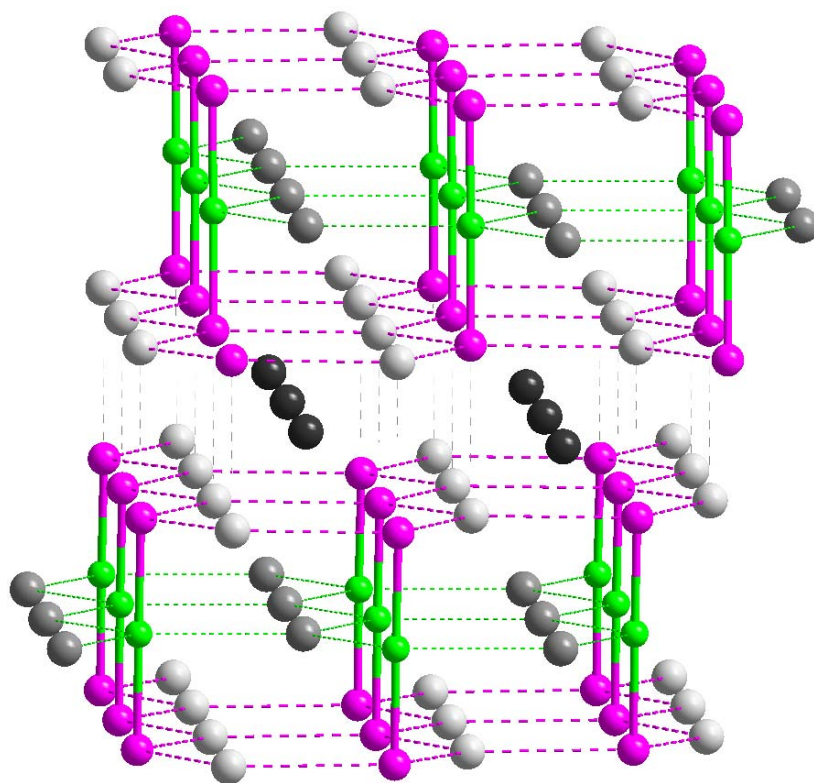|	c--	n--	-c-	-n-	--a	--b	--21
N	231	231	117	117	58	58	21
N(I>3s)	146	146	72	72	37	37	2
<I>	316.7	316.7	452.3	452.3	615.1	615.1	5.0
<I/s>	7.8	7.8	7.1	7.1	8.0	8.0	**0.8**

Fig. S2 Crystal structure of K_4ZnBi_2 built of graphite-like layers composed of K_3Zn_3 and K_3Bi_3 rings, respectively.

3.   Complete reference 24

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega,   G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03, revision D.02. Gaussian, Inc., Wallingford CT, 2004.