

Supporting Information

BaNa₂Co₇Te₃O₁₈ with distorted 2-uniform lattice (T13) showing unusual magnetic behaviors

Jinyang Li, Zhiying Zhao, Xing Huang, Meiyan Cui, and Zhangzhen He*

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

* To whom correspondence should be addressed.

E-mail: hezz@fjirsm.ac.cn

Figure S1. The photo of grown crystals.

Figure S2. The experimental and calculated XRD patterns of BaNa₂Co₇Te₃O₁₈.

Figure S3. View of the oxygen-coordination environments for (a) Na and (b) Ba atoms in BaNa₂Co₇Te₃O₁₈.

Figure S4. Topological structure of BaNa₂Co₇Te₃O₁₈ in the *ab* plane, showing (a) twisted honeycomb structure formed by Co1 ions and (b) standard honeycomb lattice formed by Co2 ions.

Figure S5. The real (χ') and imaginary (χ'') components of the ac susceptibilities for BaNa₂Co₇Te₃O₁₈ measured at an oscillating field of 3 Oe with different frequencies.

Table S1. Crystal Data and Structure Refinement for BaNa₂Co₇Te₃O₁₈ at 293 K.

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for BaNa₂Co₇Te₃O₁₈.

Table S3. Selected bond lengths and angles for BaNa₂Co₇Te₃O₁₈.

Table S4. Anisotropic displacement parameters for BaNa₂Co₇Te₃O₁₈.

Table S5. The bond valence sum (BVS) calculation of all atoms for BaNa₂Co₇Te₃O₁₈.

Experimental details:

Synthesis. Polycrystalline sample of $\text{BaNa}_2\text{Co}_7\text{Te}_3\text{O}_{18}$ can be prepared through a high-temperature solid-state reaction using high-purity chemicals of BaCO_3 (99.99%), Na_2CO_3 (99.9%), $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (99.9%) and TeO_2 (99.99%) as raw materials with a molar ratio of 1:1:7:3. The raw materials were ground fully and calcined in a muffle furnace in air at 700 °C for 50 h with several intermediate grindings. Single crystals of $\text{BaNa}_2\text{Co}_7\text{Te}_3\text{O}_{18}$ were grown by a flux method using TeO_2 and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ as a mixed flux. The mixture of polycrystalline sample of $\text{BaNa}_2\text{Co}_7\text{Te}_3\text{O}_{18}$, TeO_2 , and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ with a molar ratio of 1:5:0.3 was milled fully and homogenized thoroughly in an agate mortar by adding a certain amount of ethanol. The homogeneous mixture (~120 g) was pressed and packed into a platinum crucible ($40 \times 40 \times 45 \text{ mm}^3$). The crucible was put into a vertical cylindrical electric furnace (height 50 cm \times Φ 10 cm) with a vertical temperature gradient of 10 °C/cm (the crucible was placed at the center of furnace). After the furnace was heated in air to 1050 °C and kept at 1050 °C for 12 h to ensure complete melting of the solution, the furnace was cooled slowly to 900 °C at a rate of 1 °C /h while keeping at a constant temperature several times. Finally, the furnace was cooled to room temperature at a rate of 10 °C /h. With this procedure, the purple strip crystals of $\text{BaNa}_2\text{Co}_7\text{Te}_3\text{O}_{18}$ can be obtained by mechanical separation from the crucible and some of strip crystals reach at the size of 2.5 cm \times 0.5 cm \times 0.3 cm (Figure S1). The purity of grown crystals was checked by powder X-ray diffraction (Figure S2) performed on a Rigaku MiniFlex 600 diffractometer equipped with a diffracted monochromator set for Cu radiation with $\lambda = 1.5406 \text{ \AA}$, showing that the obtained and simulated patterns are coincident without redundant peaks.

Crystal Structure Determination. A small crystal of $\text{BaNa}_2\text{Co}_7\text{Te}_3\text{O}_{18}$ with a size of 0.2 mm \times 0.05 mm \times 0.05 mm were selected and mounted on glassy fibers for single crystal X-ray diffraction (XRD) measurements. Data collections were performed at 293 K on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The data sets were corrected for Lorentz and polarization factors as well as for absorption by Multi-scan

method [1]. The crystal structure was solved using direct methods and refined by full matrix least-squares fitting on F^2 by SHELX-14 program [2] using the Olex2² interface [3]. The final refined structure parameters were checked by the PLATON program [4]. Crystallographic data and structural parameters for the compound are summarized in Table S1-S4. The bond valence sum (BVS) calculation of all atoms for $\text{BaNa}_2\text{Co}_7\text{Te}_3\text{O}_{18}$ is listed in Table S5.

Magnetic Measurement. A single crystal sample of $\text{BaNa}_2\text{Co}_7\text{Te}_3\text{O}_{18}$ with a size of $4 \text{ mm} \times 1 \text{ mm} \times 1 \text{ mm}$ (weight $\sim 24.1 \text{ mg}$) was fixed by non-magnetic tape and placed horizontally or vertically in a plastic drinking straw. Magnetic measurements of $\text{BaNa}_2\text{Co}_7\text{Te}_3\text{O}_{18}$ were performed on a commercial Quantum Design Physical Property Measurement System (PPMS-9). The dc magnetic susceptibility was measured under an applied field of 1000 Oe from 300 to 2 K (temperature scan of 5 K/min) and the isothermal magnetization was measured at 2 K from -8 to 8 T (field scan of 0.1 T/step). Zero field-cooling (ZFC) and field-cooling (FC) magnetic susceptibilities were also measured at 0.1 T from 2 to 300 K. The ac susceptibilities were measured under an oscillating field of 0.3 Oe with different frequencies from 100 to 10000 Hz. Specific heat was measured at zero field from 300 K to 2 K by a relaxation method using a single crystal sample of $\sim 10.2 \text{ mg}$ ($\sim 2.5 \text{ mm} \times \sim 2.5 \text{ mm} \times \sim 0.27 \text{ mm}$) with N-grease. Magnetic data corrections were estimated by using Pascal constants and background correction due to the sample holders.

[1] CrystalClear, Version 1.3.5; Rigaku Corp.: The Woodlands, TX, 1999.

[2] G. M. Sheldrick, Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 3-8.

[3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, A. K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339-341.

[4] A. Spek, Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* **2003**, *36*, 7-13.



Figure S1. The photo of BaNa₂Co₇Te₃O₁₈ grown crystals.

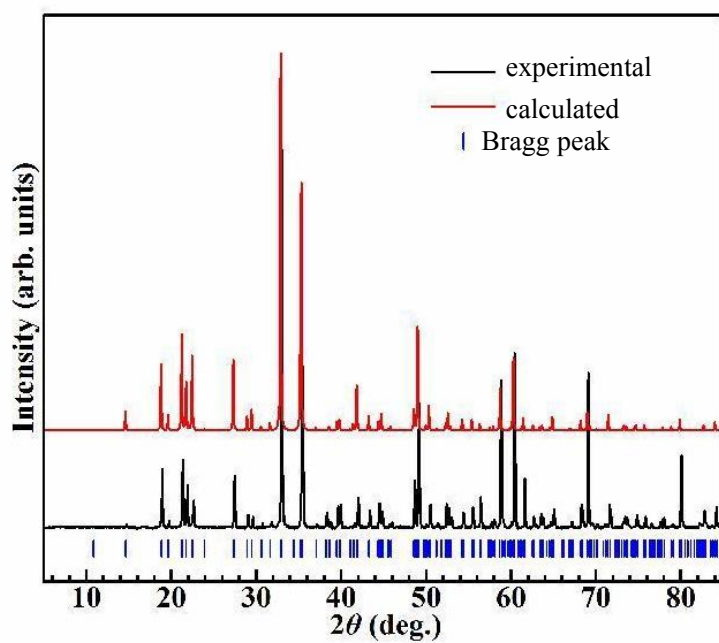


Figure S2. The experimental and calculated XRD patterns of BaNa₂Co₇Te₃O₁₈.

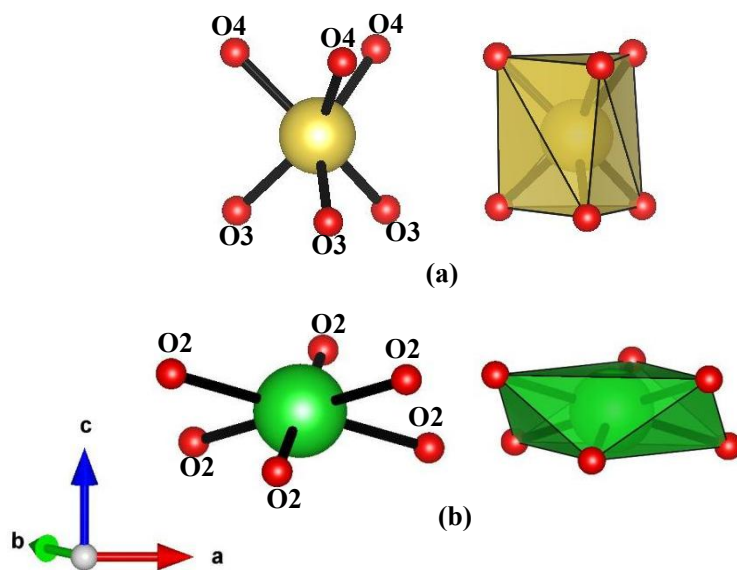


Figure S3. View of the oxygen-coordination environments (polyhedron) for (a) Na and (b) Ba atoms in $\text{BaNa}_2\text{Co}_7\text{Te}_3\text{O}_{18}$.

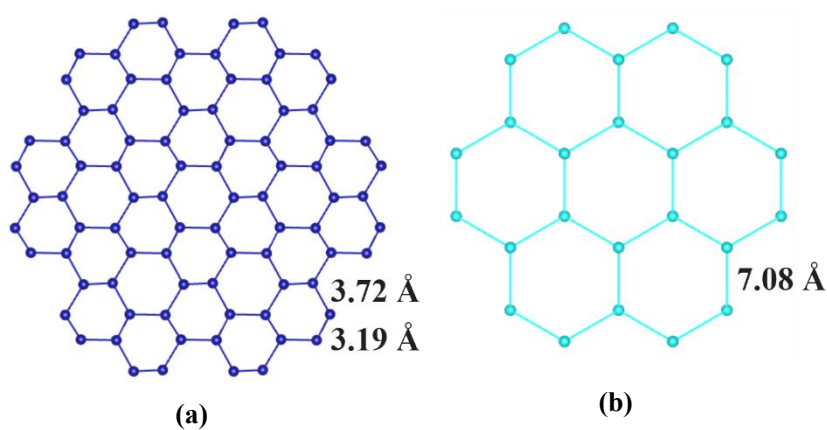


Figure S4. Topological structure of $\text{BaNa}_2\text{Co}_7\text{Te}_3\text{O}_{18}$ in the ab plane, showing (a) twisted honeycomb structure formed by Co1 ions and (b) standard honeycomb lattice formed by Co2 ions.

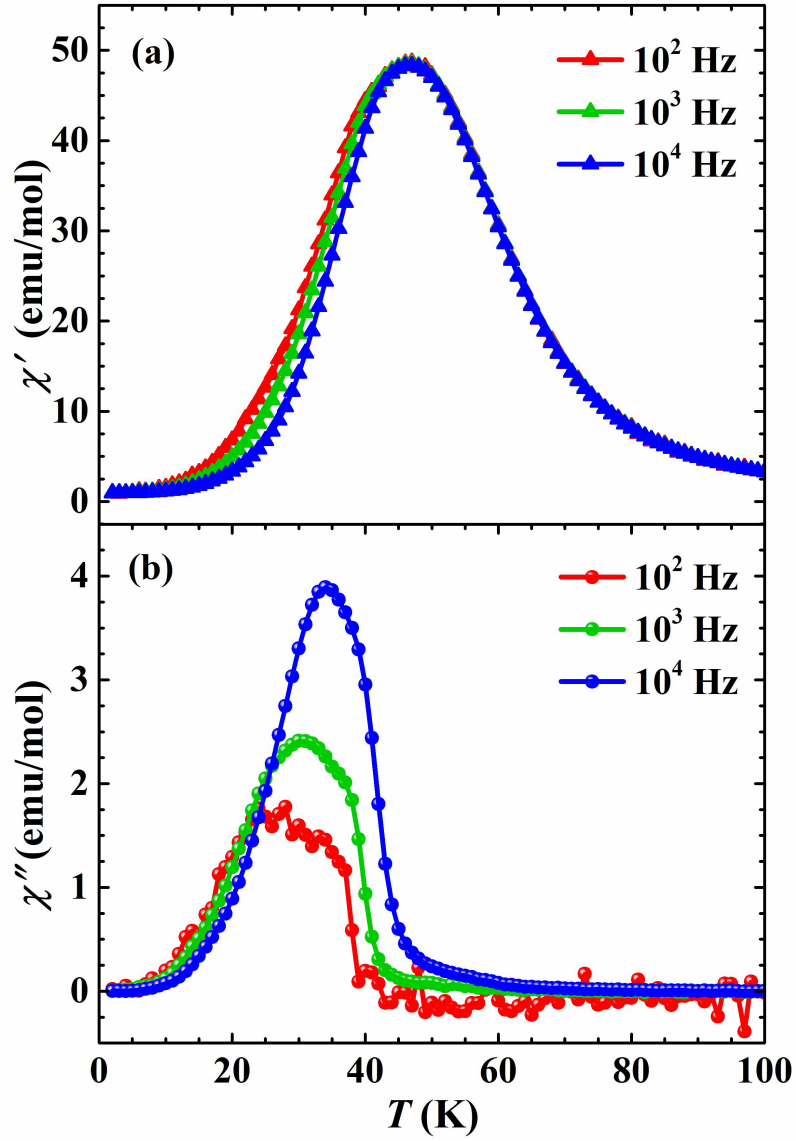


Figure S5. (a) The real (χ') and (b) imaginary (χ'') components of the ac susceptibilities for $\text{BaNa}_2\text{Co}_7\text{Te}_3\text{O}_{18}$ measured at an oscillating field of 3 Oe with different frequencies.

Table S1. Crystal Data and Structure Refinement for BaNa₂Co₇Te₃O₁₈ at 293 K.

Formula	BaNa ₂ Co ₇ Te ₃ O ₁₈
Formula weight	1266.60
Temperature/K	293(2)
Crystal system	hexagonal
Space group	<i>P</i> 6 ₃ / <i>m</i>
<i>a</i> /Å	9.4283(2)
<i>b</i> /Å	9.4283(2)
<i>c</i> /Å	9.0489(2)
α /°	90
β /°	90
γ /°	120
Volume/Å ³	696.62(3)
<i>Z</i>	2.00004
ρ_{calc} /cm ³	6.039
μ /mm ⁻¹	17.231
F(000)	1134.0
Radiation	MoK α (λ = 0.71073)
Goodness-of-fit on F ²	1.178
Final R indexes [<i>I</i> ≥ 2 σ (<i>I</i>)] ^a	R ₁ = 0.0233, wR ₂ = 0.0505
Final R indexes [all data]	R ₁ = 0.0264, wR ₂ = 0.0514

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, and $wR_2 = \{ \sum w[(F_o)^2 - (F_c)^2]^2 / \sum w[(F_o)^2]^2 \}^{1/2}$

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{BaNa}_2\text{Co}_7\text{Te}_3\text{O}_{18}$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
Co(1)	3584.6(6)	3509.9(6)	4099.6(5)	6.30(11)
Co(2)	6666.67	3333.33	7500	10.2(2)
Ba(1)	0	0	5000	15.72(14)
Na(1)	3333.33	6666.67	5777(3)	4.8(4)
Te(1)	3547.7(3)	3435.9(4)	7500	3.77(9)
O(1)	2825(5)	1120(4)	7500	8.6(6)
O(2)	2080(3)	3168(3)	5914(3)	6.7(4)
O(3)	4571(4)	5803(4)	7500	7.1(6)
O(4)	5200(3)	3862(3)	8996(3)	7.5(4)

U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Table S3. Selected bond lengths and angles for $\text{BaNa}_2\text{Co}_7\text{Te}_3\text{O}_{18}$.

Te(1)-O(3)	1.939(3)	Co(2)-O(4)#8	2.164(3)
Te(1)-O(2)#1	1.920(2)	Co(2)-O(4)#9	2.164(3)
Te(1)-O(2)	1.920(2)	Co(2)-O(4)#1	2.164(3)
Te(1)-O(4)	1.948(2)	Co(2)-O(4)#10	2.164(3)
Te(1)-O(4)#1	1.948(2)	Co(2)-O(4)	2.164(3)
Te(1)-O(1)	1.935(3)	Co(2)-O(4)#11	2.164(3)
Co(1)-O(3)#3	2.101(3)	Na(1)-O(3)#12	2.325(3)
Co(1)-O(2)#4	2.115(2)	Na(1)-O(3)#13	2.325(3)
Co(1)-O(2)	2.087(3)	Na(1)-O(3)	2.325(3)
Co(1)-O(4)#1	2.212(3)	Na(1)-O(4)#14	2.334(3)
Co(1)-O(4)#5	2.150(3)	Na(1)-O(4)#15	2.334(3)
Co(1)-O(1)#6	2.123(3)	Na(1)-O(4)#5	2.334(3)
		O(2)-Ba(1)	2.756(2)
O(3)-Te(1)-O(4)	82.89(11)	O(2)#1-Te(1)-O(4)#1	174.67(11)

O(3)-Te(1)-O(4)#1	82.89(11)	O(2)-Te(1)-O(1)	91.58(11)
O(2)#1-Te(1)-O(3)	93.59(10)	O(2)#1-Te(1)-O(1)	91.58(11)
O(2)-Te(1)-O(3)	93.59(10)	O(4)-Te(1)-O(4)#1	88.05(15)
O(2)-Te(1)-O(2)#1	96.70(15)	O(1)-Te(1)-O(3)	172.22(16)
O(2)-Te(1)-O(4)	174.67(11)	O(1)-Te(1)-O(4)	91.53(11)
O(2)#1-Te(1)-O(4)	87.54(10)	O(1)-Te(1)-O(4)#1	91.53(11)
O(2)-Te(1)-O(4)#1	87.54(10)	O(4)#8-Co(2)-O(4)#1	134.09(4)
O(3)#3-Co(1)-O(2)#4	90.41(12)	O(4)#1-Co(2)-O(4)	77.47(13)
O(3)#3-Co(1)-O(4)#1	95.09(9)	O(4)#10-Co(2)-O(4)#8	134.08(5)
O(3)#3-Co(1)-O(4)#5	74.49(11)	O(4)#8-Co(2)-O(4)#11	77.46(13)
O(3)#3-Co(1)-O(1)#6	93.47(10)	O(4)#10-Co(2)-O(4)	134.09(5)
O(2)-Co(1)-O(3)#3	169.67(10)	O(4)#11-Co(2)-O(4)#1	85.00(10)
O(2)-Co(1)-O(2)#4	95.33(12)	O(4)#7-Co(2)-O(4)#8	85.00(10)
O(2)#4-Co(1)-O(4)#5	161.53(10)	O(4)#10-Co(2)-O(4)#11	85.00(10)
O(2)-Co(1)-O(4)#5	98.14(10)	O(4)#8-Co(2)-O(4)	85.00(10)
O(2)-Co(1)-O(4)#1	76.95(9)	O(4)#11-Co(2)-O(4)	134.09(4)
O(2)#4-Co(1)-O(4)#1	84.78(10)	O(4)#10-Co(2)-O(4)#1	85.00(10)
O(2)-Co(1)-O(1)#6	95.16(10)	O(4)#10-Co(2)-O(4)#7	77.46(13)
O(2)#4-Co(1)-O(1)#6	89.51(12)	O(4)#7-Co(2)-O(4)#1	134.09(5)
O(4)#5-Co(1)-O(4)#1	86.03(10)	O(4)#7-Co(2)-O(4)	85.00(10)
O(1)#6-Co(1)-O(4)#1	169.74(11)	O(4)#7-Co(2)-O(4)#11	134.08(5)
O(1)#6-Co(1)-O(4)#5	101.74(12)		

Symmetry transformations used to generate equivalent atoms: #1 +x,+y,3/2-z; #2 +x,+y,1/2-z; #3 1-x,1-y,1-z; #4 +y,-x+y,1-z; #5 1-x,1-y,-1/2+z; #6 -y+x,+x,1-z; #7 1-y,+x-y,+z; #8 1+y-x,1-x,+z; #9 1-x,1-y,1/2+z; #10 1-y,+x-y,3/2-z; #11 1+y-x,1-x,3/2-z; #12 +y,1-x+y,1-z; #13 +y-x,1-x,+z; #14 1-y,1+x-y,+z; #15 -y+x,+x,-1/2+z; #16 +y,1-x+y,-1/2+z;

Table S4. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{BaNa}_2\text{Co}_7\text{Te}_3\text{O}_{18}$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*2U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Te(1)	3.97(14)	3.92(14)	3.14(14)	0	0	1.77(10)
Co(1)	6.5(2)	6.1(2)	5.4(2)	0.41(15)	0.63(15)	2.44(16)
Co(2)	10.1(3)	10.1(3)	10.2(6)	0	0	5.06(16)
Na(1)	4.3(6)	4.3(6)	5.8(11)	0	0	2.2(3)
O(3)	7.2(15)	2.5(14)	10.2(17)	0	0	1.4(12)
O(2)	6.4(10)	9.5(10)	4.9(10)	-2.1(9)	-2.3(8)	4.4(9)
O(4)	6.3(10)	9.5(11)	6.2(11)	-0.5(9)	-2.7(9)	3.7(9)
O(1)	12.4(16)	3.6(14)	10.1(16)	0	0	4.1(12)
Ba(1)	7.52(15)	7.52(15)	32.1(3)	0	0	3.76(7)

Table S5. The bond valence sum (BVS) calculation of all atoms for $\text{BaNa}_2\text{Co}_7\text{Te}_3\text{O}_{18}$.

Atom	BVS	Valence
Ba1	2.132	+2
Na1	1.447	+1
Co1	1.841	+2
Co2	1.675	+2
Te1	5.716	+6
O1	1.727	-2
O2	1.934	-2
O3	2.094	-2
O4	1.971	-2