Supplementary Information (SI) for Journal of Materials Chemistry C.

Supplemental Informations for A computational and Raman spectroscopic study of successive phase transitions in Co_3TeO_6 under high pressure and high temperature

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TABLE S1: Crystal structure parameters of the Rietveld refinements of the PXD data of the AP Co_3TeO_6. Monoclinic, space group $C2/c$ (No. 12), $a = 14.8009(1)$ Å, $b = 8.8380(7)$ Å, $c = 10.3429(1)$ Å, $\beta = 94.835(5)^\circ$, $V = 1348.14(2)$ Å^3, $Z = 12$,$R_p/R_{wp} = 0.81/1.07\%$.

Atom	*Position*	*x*	*y*	*z*	*Occ.*	B_{eq}(Å^2)
Co1	4*e*	0.5	−0.1891(2)	0.25	1	0.67(2)
Co2	8*f*	0.8591(8)	−0.3559(9)	0.2338(9)	1	0.76(3)
Co3	8*f*	0.5231(6)	−0.6518(9)	0.0393(7)	1	0.74(3)
Co4	8*f*	0.6638(6)	−0.2894(8)	0.0574(7)	1	0.58(5)
Co5	8*f*	0.7999(6)	−0.3641(9)	0.5730(8)	1	0.52(3)
Te1	4*b*	0	0.5	0.5	1	0.77(8)
Te2	8*f*	0.6590(2)	−0.4995(6)	0.2994(3)	1	1.01(6)
O1	8*f*	0.9318(5)	−0.3419(4)	0.5742(7)	1	0.81(7)
O2	8*f*	0.5978(1)	−0.3378(7)	0.2018(1)	1	0.95(2)
O3	8*f*	0.5991(1)	−0.6623(1)	0.1967(3)	1	0.87(3)
O4	8*f*	0.7482(5)	−0.5225(3)	0.6698(3)	1	0.75(3)
O5	8*f*	0.9347(2)	−0.5119(3)	0.3345(7)	1	0.94(5)
O6	8*f*	0.5889(7)	−0.5171(5)	0.4380(5)	1	0.89(3)
O7	8*f*	0.9289(3)	−0.6567(2)	0.5605(3)	1	0.96(8)
O8	8*f*	0.7341(3)	−0.3379(3)	0.3872(1)	1	0.86(6)
O9	8*f*	0.7282(5)	−0.6521(5)	0.3905(2)	1	0.81(2)

TABLE S2: Crystallographic parameters of the synthesized Co_3TeO_6 samples obtained at 5 GPa 1073 K, refined from the SPXD data. Trigonal, space group $R3$ (No. 146), $a = 5.1910(8)$ Å, $c = 13.8187(2)$ Å, $V = 322.46(1)$ Å^3, $Z = 3$,$R_p/R_{wp} = 5.96/7.36\%$.

Atom	*Position*	*x*	*y*	*z*	*Occ.*	B_{eq}(Å^2)
Co1	3*a*	0	0	0.1988(2)	1	0.73(4)
Co2	3*a*	0	0	0.4791(3)	1	0.70(4)
Co3	3*a*	0	0	0.6837(2)	1	0.65(3)
Te1	3*a*	0	0	−0.0121(1)	1	1.06(6)
O1	9*b*	0.1438(7)	0.1903(1)	−0.0418(3)	1	0.54(8)
O2	9*b*	0.6264(2)	−0.0107(1)	0.2779(6)	1	0.67(1)

TABLE S3: Crystallographic parameters of the synthesized Co_3TeO_6 samples obtained at 20 GPa 1473 K, refined from the SPXD data. Monoclinic, space group $P2_1/n$ (No. 14), $a = 5.0232(4)$ Å,$b = 5.1861(7)$ Å, $c = 7.1854(8)$ Å, $\beta = 94.09(1)^\circ$, $V = 186.71(1)$ Å^3, $Z = 2$,$R_p/R_{wp} = 2.77/3.58\%$.

Atom	*Position*	*x*	*y*	*z*	*Occ.*	B_{eq}(Å^2)
Co1	4*e*	0.6809(2)	0.1185(6)	0.2374(3)	1	0.51(3)
Co2	2*d*	0.5	0	0	1	0.64(5)
Te1	2*c*	0	0.5	0	1	0.46(2)
O1	4*e*	0.1517(5)	1.1783(3)	0.2105(1)	1	0.52(1)
O2	4*e*	0.5117(6)	0.5257(8)	0.1511(3)	1	0.41(2)
O3	4*e*	0.7827(2)	0.0145(7)	0.0671(6)	1	0.62(5)

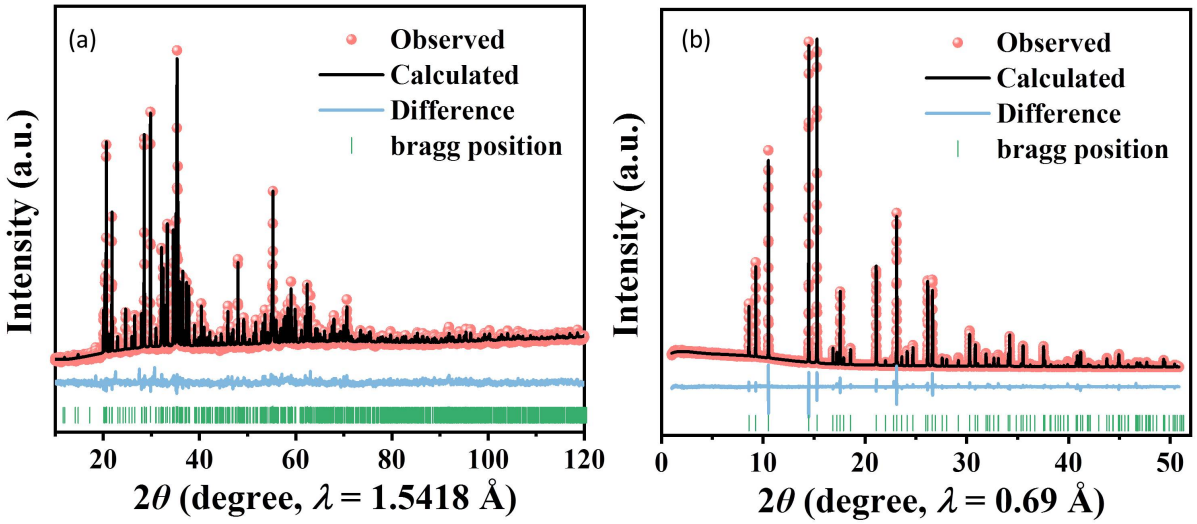

FIG. S1: Refinement of the (a) PXD data of Co_3TeO_6 in $C2/c$ and (b) SPXD data of Co_3TeO_6 in $R3$ (obtained at 5 GPa 1073 K), respectively. The experimental, calculated, difference curves, and Bragg-reflection positions are shown in red, black, blue and green, respectively.

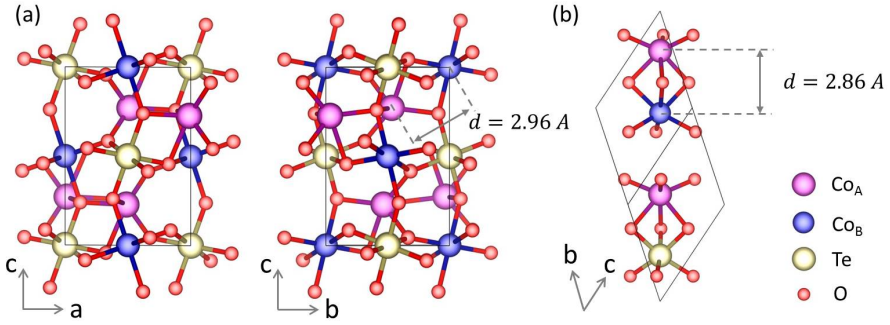

FIG. S2: The optimized unit cells of Co_3TeO_6 in (a) $P2_1/n$ and (b) $R3$ (with cell volumes $V = 202$ and 101 Å^3, respectively), with the minimum distance between Co_A and Co_B indicated.

TABLE S4: The typical structural parameters and atomic Wyckoff positions of Mn_3TeO_6 at AP ($R\bar{3}$)[1] and HP ($P2_1/n$)[2], Co_3TeO_6 at AP ($C2/c$)[3], HP ($R3$)[4,5] and of the optimized $P2_1/n$ structure[6]. Note that the B (Mn_B or Co_B) and B' (Te) sites are interchanged between Mn_3TeO_6 and Co_3TeO_6 in $P2_1/n$ structure, whose Wyckoff positions are named by choosing b as unique axis with cell choice 2[7].

system	space group	a(Å)	b(Å)	c(Å)	β(°)	atom	x	y	z
Mn_3TeO_6	$P2_1/n$	5.295	5.453	7.809	90.370	Mn_A (4e)	0.0107	0.0475	0.2407
						Mn_B (2c)	0	0.5	0
						Te (2d)	0.5	0	0
						O1 (4e)	0.3383	0.3018	0.0831
						O2 (4e)	0.1946	0.8243	0.0463
						O3 (4e)	−0.1308	0.4303	0.2707
	$R\bar{3}$	8.867	-	10.673	-	Mn (18f)	0.0384	0.2643	0.2130
						Te1 (3b)	0	0	0.5
						Te2 (3a)	0	0	0
						O1 (18f)	0.0307	0.1963	0.4028
						O2 (18f)	0.1828	0.1562	0.1105
Co_3TeO_6	$C2/c$	14.817	8.851	10.363	94.900	Co1 (4e)	0.5	−0.1878	0.25
						Co2 (8f)	0.8583	−0.3540	0.2336
						Co3 (8f)	0.5231	−0.6546	0.0400
						Co4 (8f)	0.6647	−0.2935	0.0550
						Co5 (8f)	0.7968	−0.3634	0.5724
						Te1 (4b)	1.0	−0.5	0.5
						Te2 (8f)	0.6614	−0.4985	0.3004
						O1 (8f)	0.9274	−0.3351	0.5611
						O2 (8f)	0.5935	−0.3450	0.2024
						O3 (8f)	0.6030	−0.6554	0.1980
						O4 (8f)	0.7484	−0.5267	0.6687
						O5 (8f)	0.9293	−0.5144	0.3377
						O6 (8f)	0.5818	−0.5117	0.4377
						O7 (8f)	0.9269	−0.6591	0.5662
						O8 (8f)	0.7377	−0.3503	0.3932
						O9 (8f)	0.7272	−0.6611	0.3887
	$R3$	5.190	-	13.820	-	Co1 (3a)	0	0	0.3688
						Co2 (3a)	0	0	0.6490
						Co3 (3a)	0	0	0.8609
						Te (3a)	0	0	0.1606
						O1 (9b)	0.2870	−0.0050	0.2470
						O2 (9b)	0.6690	−0.0220	0.7570
	$P2_1/n$	5.240	5.167	7.461	90.346	Co_A (4e)	0.4879	0.4668	0.2288
						Co_B (2d)	0.5	0	0
						Te (2c)	0	0.5	0
						O1 (4e)	0.1205	0.5895	0.2398
						O2 (4e)	0.6757	0.6653	0.0430
						O3 (4e)	0.8407	0.1853	0.0849

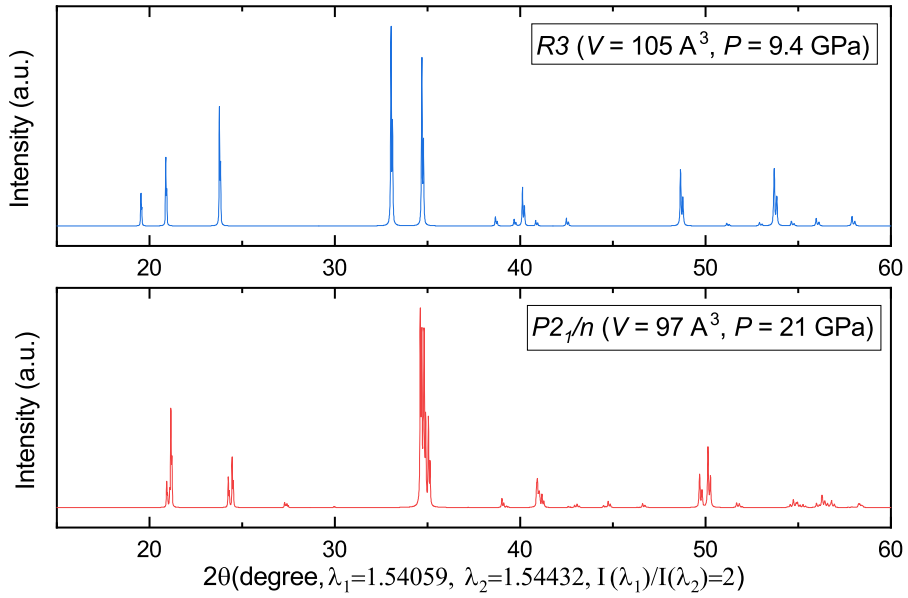

FIG. S3: The simulated X-ray powder diffraction patterns of Co_3TeO_6 in $R3$ and $P2_1/n$, respectively, by VESTA[8].

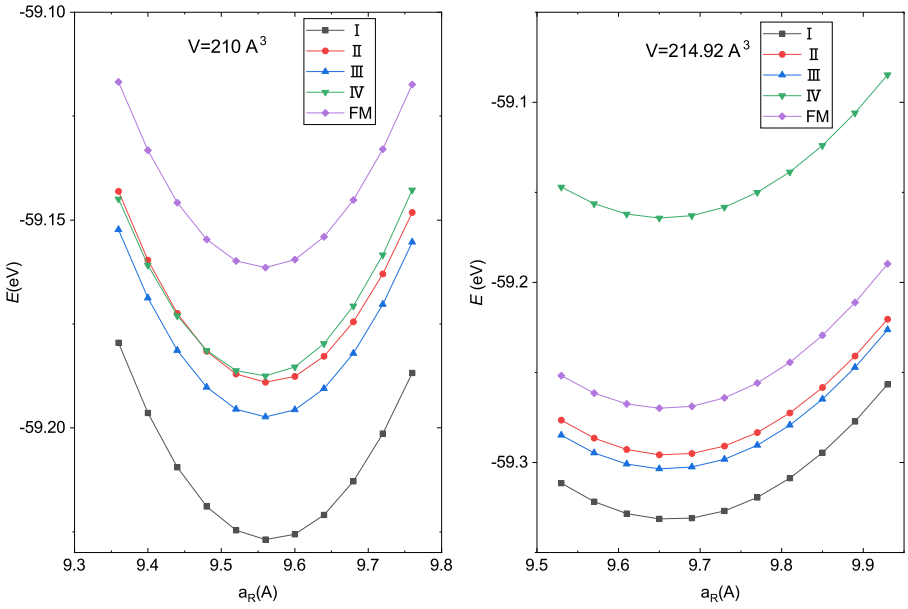

FIG. S4: The variation of total energies of Co_3TeO_6 in $R3$ phase with lattice constant a_R in different magnetic structures. The volume of the unit cell is fixed at (a) $V = 210$ and (b) $V = 214.92$ Å^3, respectively.

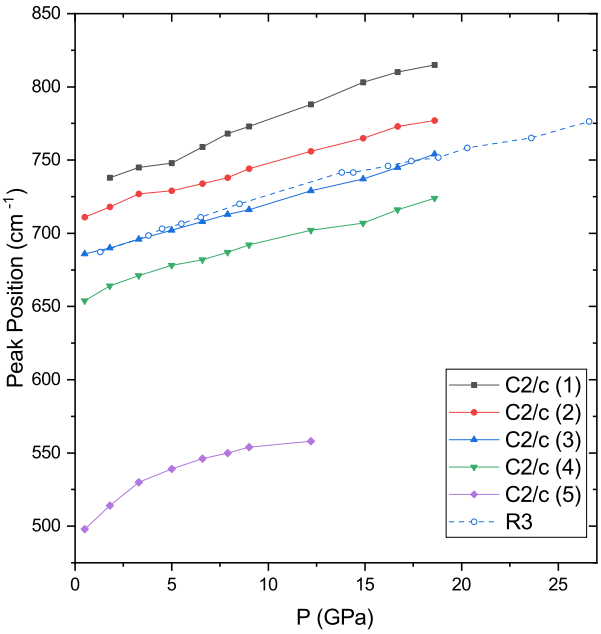

FIG. S5: The pressure dependence of the phonon frequencies of Raman spectrum of Co_3TeO_6 in $C2/c$ and $R3$ phases, obtained from Fig.6 in main text. The frequencies of five highest peaks of $C2/c$ are shown.

TABLE S5: The maximum change of lattice parameters of $A_2BB'O_6$ with small A-site cations extracted from experimental reports. ΔT is the measured temperature range.

system	space group	P (GPa)	$T_N(K)$	$\Delta a(Å)$	$\Delta b(Å)$	$\Delta c(Å)$	$\Delta\beta(^\circ)$	$\Delta T(K)$	$\Delta V(Å^3)$	$\Delta\bar{d}_{B-O}(Å)$	$\Delta\bar{d}_{B'-O}(Å)$
Mn_3ReO_6[9]	$P2_1/n$	5	110, 50	0.008	0.015	0.010	0.04	[5, 300]	1.22	-	-
Mn_2FeReO_6[10]	$P2_1/n$	5	520, 75 (FM)	0.012	0.012	0.017	0.15	[4, 300]	1.22	0.03	0.03
Mn_2CoReO_6[11]	$P2_1/n$	8	94	0.008	0.006	0.002	0.09	[2, 130]	0.60	-	-
Mn_3WO_6[12]	$R3$	8	58	0.004	-	0.02	-	[5, 100]	0.70	0.1	0.02
Mn_2InSbO_6[13]	$R3$	5	38, 17, 8	0.001	-	0.001	-	[4, 30]	-	0.08	0.09*
Mn_2FeMoO_6[14]	$P2_1/n$	8	194, 45	0.011	0.010	0.011	0.01	[10, 300]	1.14	0.09	0.14
Mn_3TeO_6[1]	$R\bar{3}$	AP	23	0.016	-	0.023	-	[5, 295]	-	0.01	0.00
Co_3TeO_6[15]	$C2/c$	AP	26, 17.4	0.028	0.006	0.015	0.18	[1.6, 295]	-	0.10	0.04
Ni_3TeO_6[16]	$R3$	AP	54	0.008	-	0.02	-	[15, 300]	-	0.04	-
Co_3TeO_6[17]	$R3$	5	58, 24	0.01	-	0.006	-	[5, 90]	0.20	0.01	0.01
Ni_2InSbO_6[18]	$R3$	AP	76	0.006	-	0.007	-	[1.7, 295]	-	0.01	0.02
Ni_2ScSbO_6[18]	$R3$	AP	60	0.005	-	0.007	-	[1.7, 295]	-	0.03	0.03

* Measured between 2 and 100 K.

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