Supporting Information

Enhancement of Ferroelectricity for Orthorhombic $(Tb_{0.861}Mn_{0.121})MnO_{3-\delta}$ by Copper Doping

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1. The refinement details of the X-ray diffraction data for C1 to C7

The Powder X-ray powder diffraction data collected at room temperature for C1 to C7 and neutron diffraction data collected at 300K for C5 are refined using GSAS software. The refinement details listed in Table S1 and S2. The corresponding Rietveld plots are shown in Figure S1, S2, …, S7. In all Rietveld plots the symbol + represents the observed value, the red solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions, and the difference curve is shown as blue color line at the bottom of the figure.

It should be mentioned that the refinement for multiphase is very difficult. Usually for the minor phase, only lattice parameters are refined. The atom's coordination is not refined. Of cause the ratio among the different phases should be refined.

Table S1 Rietveld refinement details of the X-ray diffraction data for C1, C2, C3 and C4 in *Pnma*

	C1	C2	C3	C4
Lattice parameter (Å)	a=5.74291(10), b=7.42546(11), c=5.29501(8)	a=5.74592(9), b=7.43082(12), c=5.30285(9)	a=5.74924(12), b=7.43126(10), c=5.30653(8)	a=5.75244(9), b=7.4240(10), c=5.30256(8)
Atom	x, y, z	x, y, z	x, y, z	x, y, z
Tb/Mn/Cu1[a]	0.0737(3), 0.2500, 0.9821(2)	0.0743(3), 0.2500, 0.9837(3)	0.0744(4), 0.2500 0.9843(1)	0.0742(3), 0.2500, 0.9831(3)
Mn/Cu2[b]	0.0000, 0.0000, 0.5000	0.0000, 0.0000, 0.5000	0.0000, 0.0000, 0.5000	0.0000, 0.0000, 0.5000
O1	0.4532(3), 0.2500, 0.1068(3)	0.4551(2), 0.2500, 0.0992(2)	0.4483(3), 0.2500, 0.0983(3)	0.4499(2), 0.2500, 0.1017(8)
O2	0.3358(3), 0.0479(3), 0.7278(3)	0.3259(3), 0.0498(2), 0.7158(3)	0.3329(3), 0.0520(3), 0.7126(3)	0.3292(3), 0.0514(2), 0.7183(3)
R factor[c]	R_{wp}=0.019, R_p=0.011	R_{wp}=0.019, R_p=0.011	R_{wp}=0.020, R_p=0.012	R_{wp}=0.028, R_p=0.024

[a]The occupancy of Tb/Mn/Cu1 is 0.861/0.121/0.000 for C1, 0.861/0.096/0.025 for C2, 0.861/0.081/0.040 for C3, and 0.861/0.081/0.040 for C4 .

[b]The occupancy of Mn/Cu2 is 1.000/0.000 for C1, 1.000/0.000 for C2, 0.990/0.010 for C3, and 0.965/0.035 for C4.

[c]R_p is sum($|I_0-I_C|$)/sum(I_0), and R_{wp} is weighted R factors for X-ray diffraction data.

Table S2 Rietveld refinement details of the X-ray diffraction data for C5, C6 and C7

	C5[f,g]	C6[g]	C7[g]
Phase 1	$Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$	$Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$	$Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$
Space group	*Pnma*	*Pnma*	*Pnma*
Lattice parameter (Å)	a= 5.75520(9), b= 7.41535(11), c= 5.29917(8)	a=5.75805(9), b= 7.40974(11), c= 5.29686(8)	a=5.75809(9), b= 7.40975(11), c= 5.29690(8)
Atom	x, y, z	x, y, z	x, y, z
Tb/Mn/Cu1[a]	0.0758(3), 0.2500, 0.9825(3)	0.0761(3), 0.2500, 0.9816(3)	0.0761(3), 0.2500, 0.9816(3)
Mn/Cu2[b]	0.0000, 0.0000, 0.5000	0.0000, 0.0000, 0.5000	0.0000, 0.0000, 0.5000
O1	0.4525(3), 0.2500, 0.0994(3)	0.4340(3), 0.2500, 0.0864(3)	0.4340(3), 0.2500, 0.0864(3)
O2	0.3348(3), 0.0564(3), 0.7065(3)	0.3291(3), 0.0572(3), 0.7081(3)	0.3291(3), 0.0572(3), 0.7081(3)
Phase 2	$Mn_{3-x-y}Tb_xCu_yO_4$	$Mn_{3-x-y}Tb_xCu_yO_4$	$Mn_{3-x-y}Tb_xCu_yO_4$
Space group	$I4_1/amd$	$I4_1/amd$	$I4_1/amd$
Lattice parameter (Å)	a=5.76768(8), c=9.44339(8)	a=5.77593(8), c=9.44483(8)	a=5.78760(8), c=9.46440(8)
Mn/Tb/Cu1[c]	0.0000, 0.2500, 0.8750(3)	0.0000, 0.2500, 0.8750(3)	0.0000, 0.2500, 0.8750(3)
Mn/Tb/Cu2	0.0000, 0.5000, 0.5000	0.0000, 0.5000, 0.5000	0.0000, 0.5000, 0.5000
O	0.0000, 0.4746(3), 0.2637(3)	0.0000, 0.4746(3), 0.2637(3)	0.0000, 0.4746(3), 0.2637(3)
Phase 3		Tb_2CuO_4[d]	Tb_2CuO_4[d]
Space group		*I4/mmm*	*I4/mmm*
Lattice parameter (Å)		*a*=3.91686(8), *b*=3.91686(8), *c*=11.72331(13)	*a*=3.91686(8), *b*=3.91686(8), *c*=11.72331(13)
Atom		x, y, z	x, y, z
Eu		0.0000, 0.0000, 0.3507(3)	0.0000, 0.0000, 0.3507(3)
Cu		0.0000, 0.0000, 0.0000	0.0000, 0.0000, 0.0000
O1		0.0000, 0.5000, 0.0000	0.0000, 0.5000, 0.0000
O2		0.0000, 0.0000, 0.1711(3)	0.0000, 0.0000, 0.1711(3)
Phase 4		CuO	CuO
Space group		*C2/c*	*C2/c*
Lattice parameter(Å)		*a*=4.69576(9), *b*=3.41800(8), *c*=5.12561(9), β=99.43(1)^o	*a*=4.67877(9), *b*=3.42702(8), *c*=5.12876(9), β=99.43(1)^o
Atom		x, y, z	x, y, z
Cu		0.2500, 0.2500, 0.000	0.2500, 0.2500, 0.000
O		0.0000, 0.4181(3), 0.2500	0.0000, 0.4181(3), 0.2500
R factor[e]	R_{wp}=0.021,R_p=0.011	R_{wp}=0.026,R_p=0.013	R_{wp}=0.031,R_p=0.015

[a]The occupancy of Tb/Mn/Cu1 is 0.861/0.081/0.040 for C5, C6, and C7

[b]The occupancy of Mn/Cu2 is 0.940/0.060 for C5, 0.920/0.080 C6and C7.

[c]The occupancy of Mn/Tb/Cu1 and Mn/Tb/Cu2 is set to 0.975/0.005/0.02.

[d]The atom coordination for Tb_2CuO_4 is referenced to $Sm_{2-x}Sr_xNiO_{4+\delta}$ with the same structure (H. Lou et al, *J. Mater. Chem.* 1997, 7, 2097.)

[e] R_p is sum($|I_0-I_C|$)/sum(I_0), and R_{wp} is weighted R factors for X-ray diffraction data.

[f]The neutron diffraction data for C5 at 300K were also refined well with the parameters listed in the Table S2.

[g]The ratios of Phase 1: Phase 2: Phase 3: Phase 4 are 72.88:1.00:0.00:0.00 for C5, 268.17:1.00:3.75:67.15 for C6, and 78.24: 1.00: 0.17: 38.32 for C7.

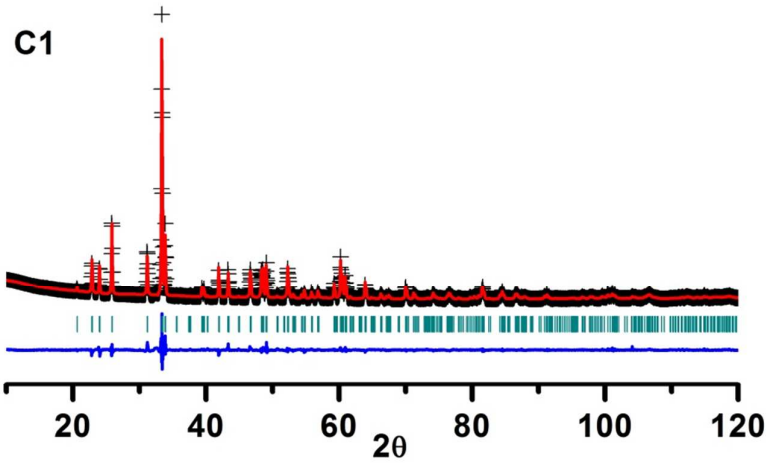

Figure S1 Rietveld plots of powder X-ray diffraction patterns (λ_1=1.5405 Å and λ_2=1.5443 Å) for C1 at room temperature.

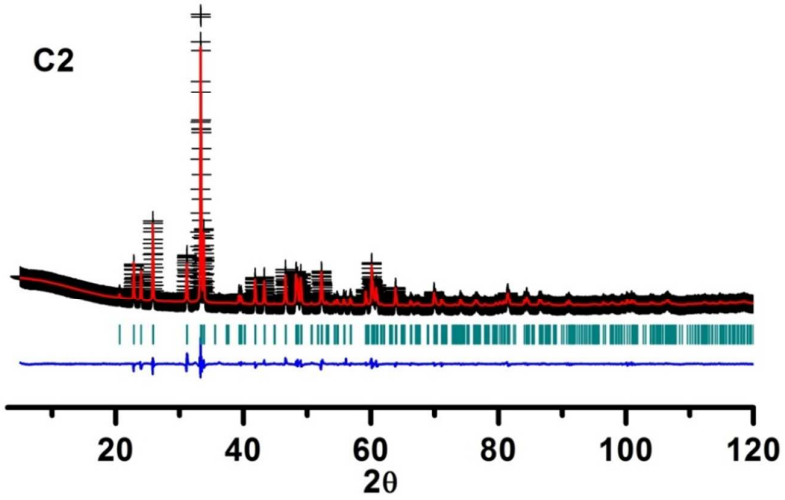

Figure S2 Rietveld plots of powder X-ray diffraction patterns (λ_1=1.5405 Å and λ_2=1.5443 Å) for C2 at room temperature.

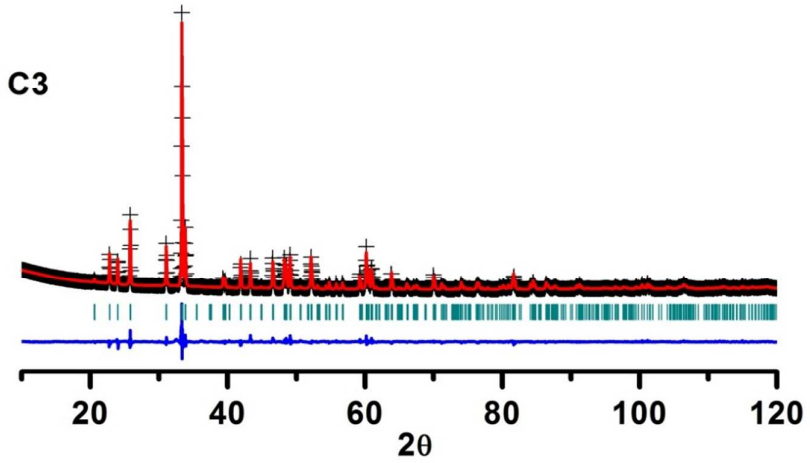

Figure S3 Rietveld plots of powder X-ray diffraction patterns (λ_1=1.5405 Å and λ_2=1.5443 Å) for C3 at room temperature.

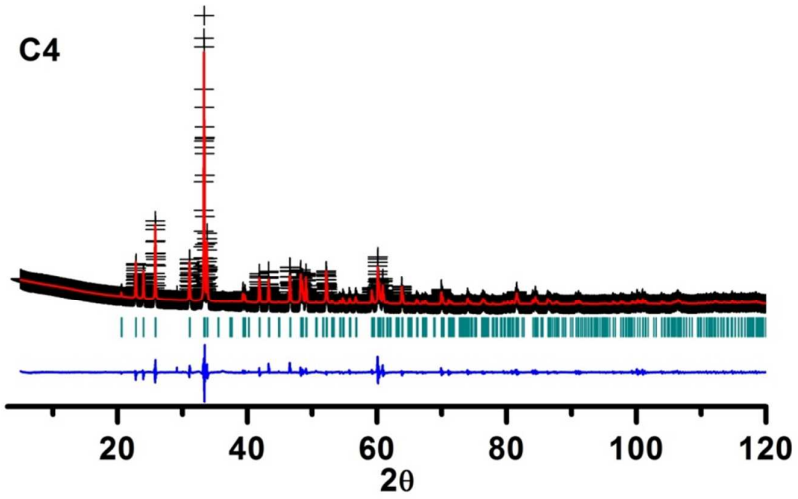

Figure S4 Rietveld plots of powder X-ray diffraction patterns (λ_1=1.5405 Å and λ_2=1.5443 Å) for C4 at room temperature.

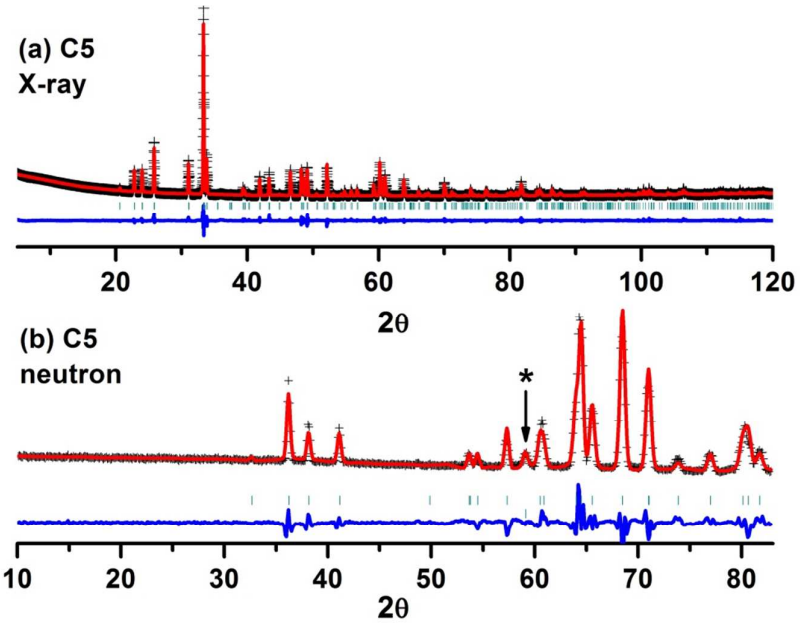

Figure S5. Rietveld plot of the X-ray (a) and neutron (b) diffraction data for C5 around room temperature.

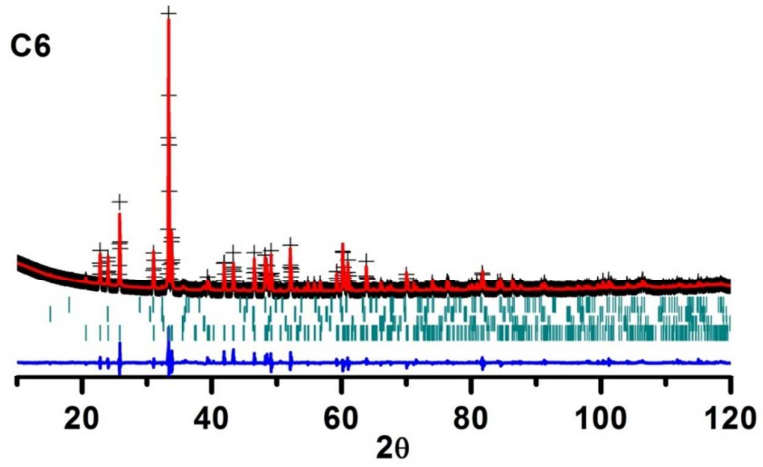

Figure S6 Rietveld plots of powder X-ray diffraction patterns (λ_1=1.5405 Å and λ_2=1.5443 Å) for C6 at room temperature. The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (the fourth line (from upper to low)), CuO (the third line), Tb_2CuO_4 (the second line), $Mn_{3-x-y}Tb_xCu_yO_4$ (the first line), and the difference curve is shown at the bottom of the figure.

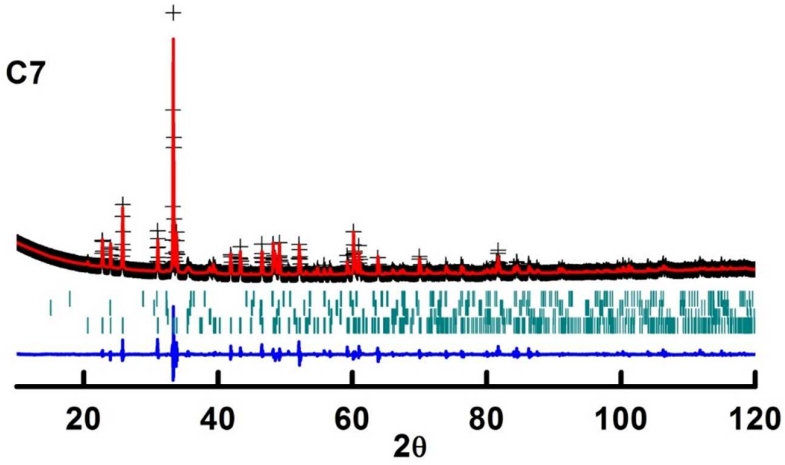

Figure S7a Rietveld plots of powder X-ray diffraction patterns (λ_1=1.5405 Å and λ_2=1.5443 Å) for C7 at room temperature. The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (the fourth line (from upper to low)), CuO (the third line), Tb_2CuO_4 (the second line), $Mn_{3-x-y}Tb_xCu_yO_4$ (the first line), and the difference curve is shown at the bottom of the figure.

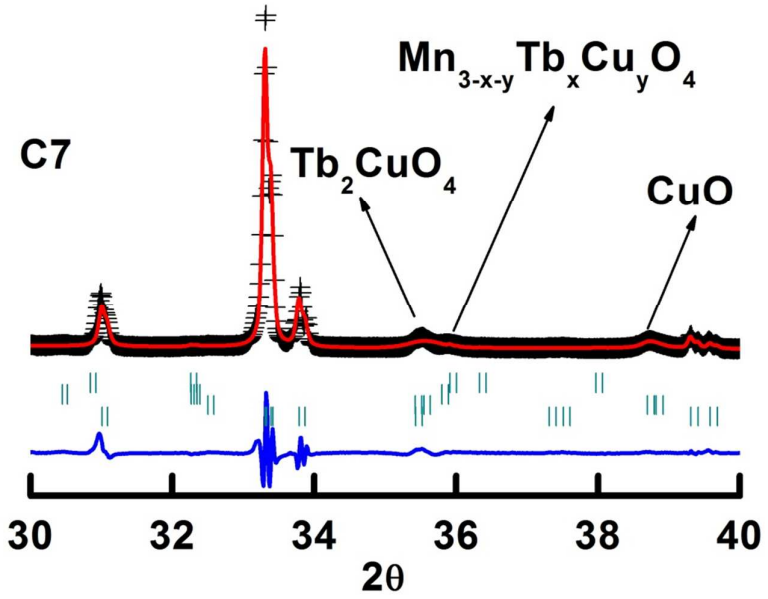

Figure S7b Enlarged figure of Figure S7. The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (the fourth line (from upper to low)), CuO (the third line), Tb_2CuO_4 (the second line), $Mn_{3-x-y}Tb_xCu_yO_4$(the first line), and the difference curve is shown at the bottom of the figure.

2. The X-ray diffraction data for $Mn_{3-x}Tb_xO_4$ and $Mn_{3-y}Cu_yO_4$

Because the neutron diffraction data for C3 and C5 show there is $Mn_{3-x-y}Tb_xCu_yO_4$ existed as impurity in the samples (although it is hard to see from the X-ray diffraction data), the samples with the nominal formula $Mn_{3-x}Tb_xO_4$ (x=0.00, 0.01, 0.02, 0.04, 0.06, 0.08, 0.10) and $Mn_{3-y}Cu_yO_4$ (y=0.00, 0.01, 0.02, 0.04, 0.06, 0.08) were synthesized at the same condition used for the preparation of $(Tb_{0.861}Mn_{0.121})Mn_{1-x}Cu_xO_{3-\delta}$ to check if magnetic peak around 80 K is related to $Mn_{3-x-y}Tb_xCu_yO_4$. The X-ray diffraction data are presented in Figure S8a and S8b. The magnetic and dielectric property of one pure sample is shown in Figure S8c and S8d in next section.It is found that for $Mn_{3-x}Tb_xO_4$, only the sample with x=0.00 is one phase (Mn_3O_4 in space group $I4_1/amd$), all others are two phase (Mn_3O_4 and $TbMnO_3$). This result indicates that only very less Tb (less than 0.01) can be doped into Mn_3O_4.

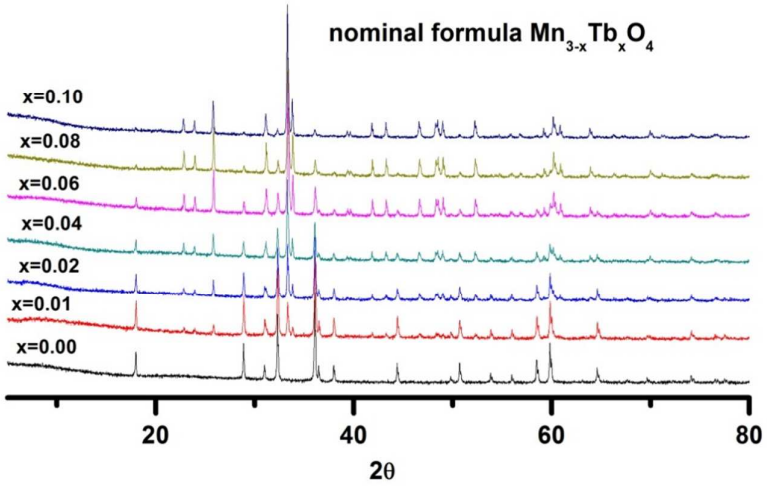

Figure S8a X-ray diffraction data for the samples with the nominal formula $Mn_{3-x}Tb_xO_4$ (x=0.00, 0.01, 0.02, 0.04, 0.06, 0.08, 0.10).

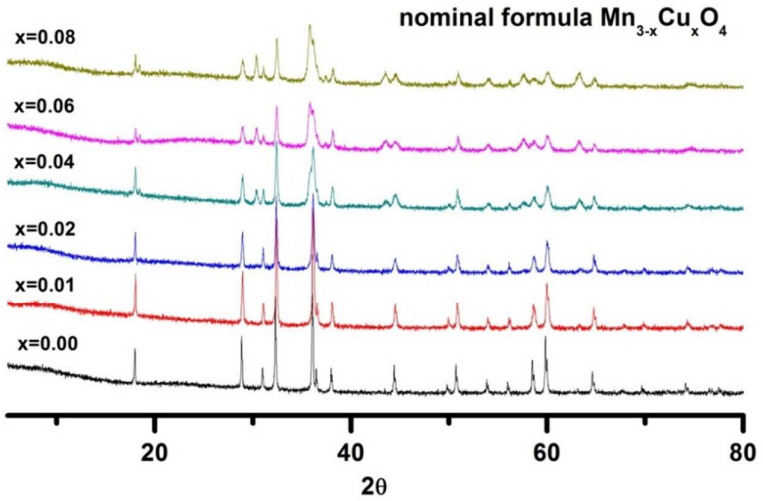

Figure S8b X-ray diffraction data for the samples with the nominal formula $Mn_{3-y}Cu_yO_4$ (y=0.00, 0.01, 0.02, 0.04, 0.06, 0.08).

However, for $Mn_{3-y}Cu_yO_4$, three samples (x=0.00, 0.01, and 0.02) are one phase (Mn_3O_4 in space group $I4_1/amd$), and the others are two phases ($CuMn_2O_4$ in space group $Fd3m$ and Mn_3O_4). This means some Cu can be doped into Mn_3O_4.

3. The magnetic and dielectric property of $Mn_{3-x}Cu_xO_4$ (x=0.02)

As confirmed in the section 2, some Cu can be doped into Mn_3O_4 to form solid solution $Mn_{3-x}Cu_xO_4$. One pure phase sample $Mn_{3-x}Cu_xO_4$ (x=0.02) was used to study the magnetic and dielectric property of $Mn_{3-x}Cu_xO_4$. The corresponding data is shown in Figure S8c and S8d. It is found that two peaks appeared in the temperature dependency of χ_{mol} for $Mn_{2.98}Cu_{0.02}O_4$. One is around 40K and the other is around 80 K. It is believed that the peak around 80K for the samples C3, C4, and C5 can be attributed to the $Mn_{3-x}Cu_xO_4$. The temperature dependent dielectric constant of $Mn_{2.98}Cu_{0.02}O_4$ was also measured. No peak around 40 K was found. Therefore, the dielectric constant peak around 40K for C3 to C5 is for the main phase $(Tb_{0.861}Mn_{0.121})Mn_{1-x}Cu_xO_{3-\delta}$.

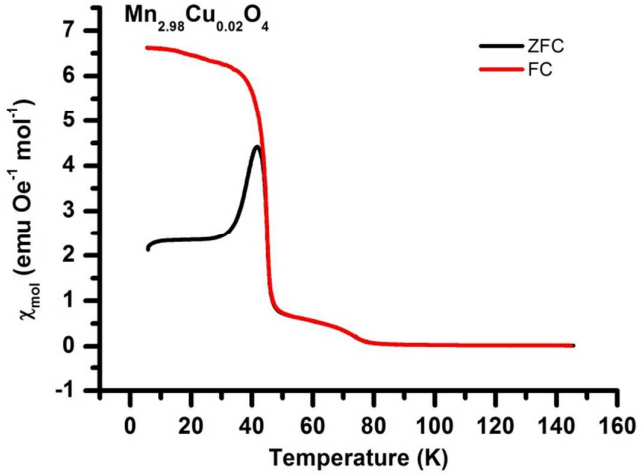

Figure S8c Temperature dependency of χ_{mol} for $Mn_{2.98}Cu_{0.02}O_4$.

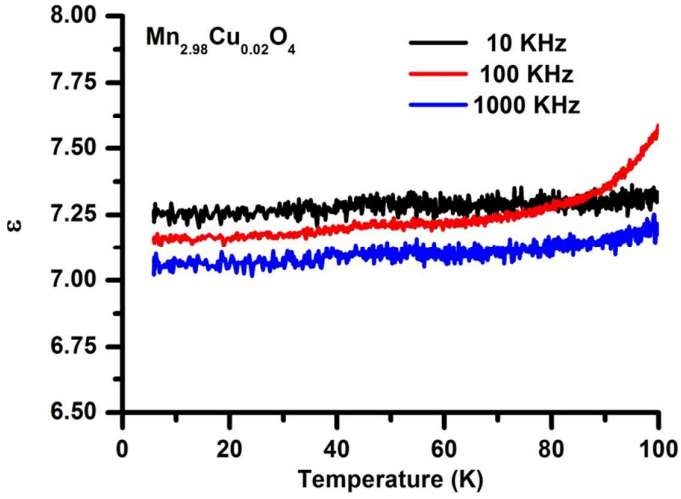

Figure S8d The dielectric property of $Mn_{2.98}Cu_{0.02}O_4$

4. The refinement details of the neutron diffraction data for C3 at selected temperatures

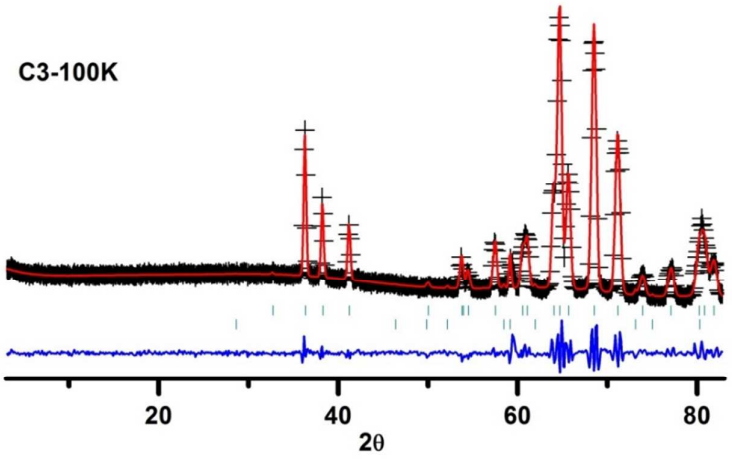

Figure S9 Rietveld plots of powder neutron diffraction patterns (λ=2.4270 Å) for C3 at 100 K. The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (upper one), $Mn_{1-x-y}Tb_xCu_yO_4$ (lower one), and the difference curve is shown at the bottom of the figure.

Table S3 Rietveld refinement details of the neutron diffraction data for C3 at 100 K

Space group	Pnma	
Lattice parameter (Å)	a=5.74416(10), b=7.41455(11), c=5.30688(8)	
Atom	x, y, z	Occupancy
Tb/Mn/Cu1	0.0814(3), 0.2500, 0.9826(2)	0.861/0.081/0.040
Mn/Cu2	0.0000, 0.0000, 0.5000	0.990/0.010
O1	0.4665(3), 0.2500, 0.1039(3)	1.000
O2	0.3190(3), 0.0503(3), 0.7041(3)	1.000
Phase 2		
Space group	$I\,4_1/a\,m\,d$	
Lattice parameter (Å)	a=5.76663(11), c=9.44201(12)	
Atom	x, y, z	Occupancy
Mn/Tb/Cu[b]	0.0000, 0.2500, 0.8750	0.975/0.005/0.02
Mn/Tb/Cu	0.0000, 0.5000, 0.5000	0.975/0.005/0.02
O	0.0000, 0.4746(9), 0.2637(8)	1.00
R factor[a]	R_{wp}=0.038, R_p=0.026	

[a] R_p is sum($|I_0-I_C|$)/sum(I_0), and R_{wp} is weighted R factors for X-ray diffraction data.
[b] It is difficult to know the ratio of Mn:Tb:Cu, the value is a guessed one according to the experiments shown below.

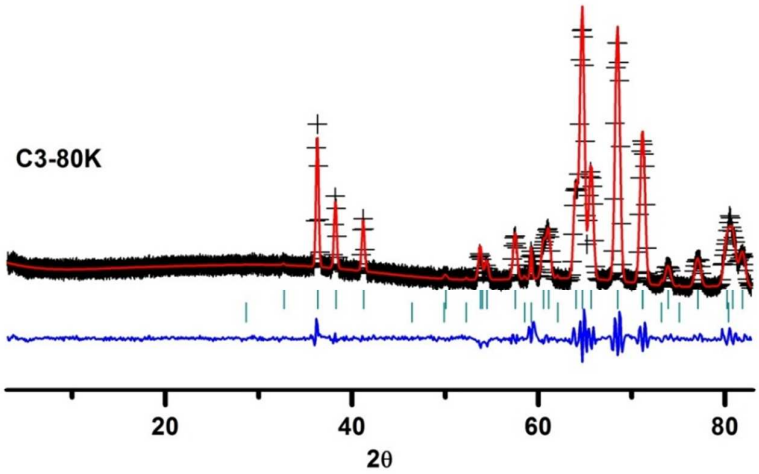

Figure S10 Rietveld plots of powder neutron diffraction patterns (λ=2.4270 Å) for C3 at 80 K. The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (upper one), $Mn_{1-x-y}Tb_xCu_yO_4$ (lower one), and the difference curve is shown at the bottom of the figure.

Table S4 Rietveld refinement details of the neutron diffraction data for C3 at 80 K

Space group	Pnma	
Lattice parameter (Å)	a=5.74114(10), b=7.41451(11), c=5.30893(8)	
Atom	x, y, z	Occupancy
Tb/Mn/Cu1	0.0807(3), 0.2500, 0.9827(2)	0.861/0.081/0.040
Mn/Cu2	0.0000, 0.0000, 0.5000	0.990/0.010
O1	0.4673(3), 0.2500, 0.1044(3)	1.000
O2	0.3189(3), 0.0504(3), 0.7041(3)	1.000
Phase 2		
Space group	$I4_1/amd$	
Lattice parameter (Å)	a=5.76223(9), c=9.42598(8)	
Atom	x, y, z	Occupancy
Mn/Tb/Cu[b]	0.0000, 0.2500, 0.8750	0.975/0.005/0.02
Mn/Tb/Cu	0.0000, 0.5000, 0.5000	0.975/0.005/0.02
O	0.0000, 0.4746, 0.2637	1.00
R factor[a]	R_{wp}=0.037, R_p=0.025	

[a]R_p is sum($|I_0-I_C|$)/sum(I_0), and R_{wp} is weighted R factors for X-ray diffraction data.
[b]It is difficult to know the ratio of Mn:Tb:Cu, the value is a guessed one according to the experiments shown below.

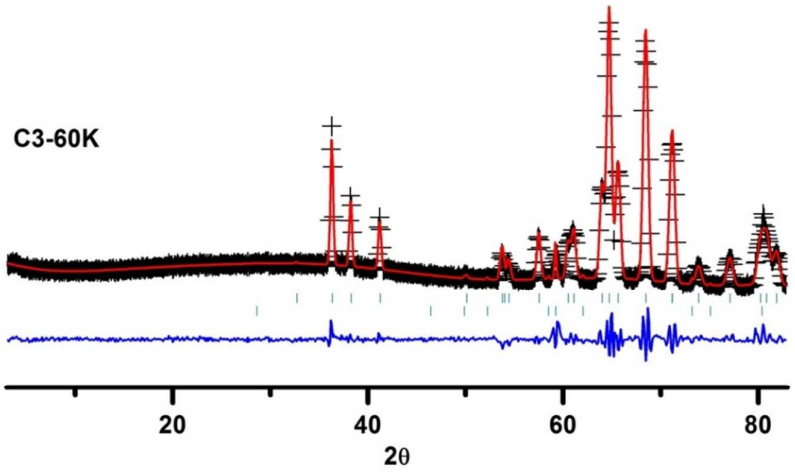

Figure S11 Rietveld plots of powder neutron diffraction patterns (λ=2.4270 Å) for C3 at 60 K. The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (upper one), $Mn_{1-x-y}Tb_xCu_yO_4$ (lower one), and the difference curve is shown at the bottom of the figure.

Table S5 Rietveld refinement details of the neutron diffraction data for C3 at 60K

Space group	Pnma	
Lattice parameter (Å)	a=5.73781(10), b=7.41397(11), c=5.31058(8)	
Atom	x, y, z	Occupancy
Tb/Mn/Cu1	0.0782(3), 0.2500, 0.9831(2)	0.861/0.081/0.040
Mn/Cu2	0.0000, 0.0000, 0.5000	0.990/0.010
O1	0.4664(3), 0.2500, 0.1057(3)	1.000
O2	0.3199(3), 0.0505(3), 0.7049(3)	1.000
Phase 2		
Space group	$I4_1/amd$	
Lattice parameter (Å)	a=5.76094(9), c=9.42933(8)	
Atom	x, y, z	Occupancy
Mn/Tb/Cu[b]	0.0000, 0.2500, 0.8750	0.975/0.005/0.02
Mn/Tb/Cu	0.0000, 0.5000, 0.5000	0.975/0.005/0.02
O	0.0000, 0.4746, 0.2637	1.00
R factor[a]	R_{wp}=0.039, R_p=0.026	

[a]R_p is sum($|I_0-I_C|$)/sum(I_0), and R_{wp} is weighted R factors for X-ray diffraction data.
[b]It is difficult to know the ratio of Mn:Tb:Cu, the value is a guessed one according to the experiments shown below.

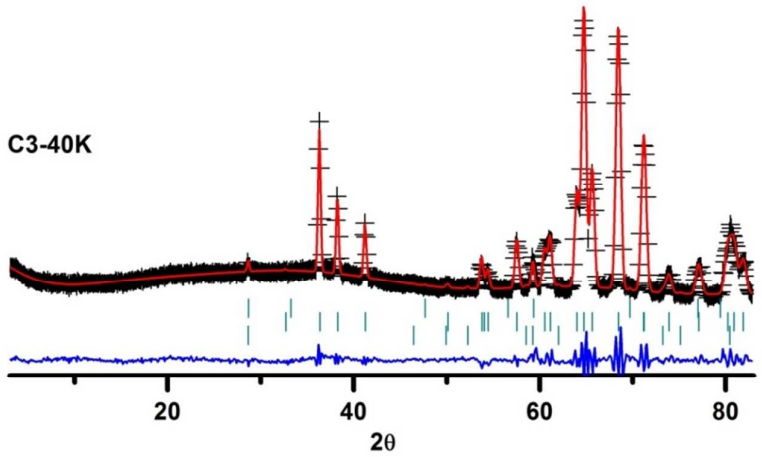

Figure S12 Rietveld plots of powder neutron diffraction patterns (λ=2.4270 Å) for C3 at 40 K. The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (middle one), nuclear (lower one) and magnetic (upper one) phase of $Mn_{1-x-y}Tb_xCu_yO_4$, and the difference curve is shown at the bottom of the figure.

Table S6 Rietveld refinement details of the neutron diffraction data for C3 at 40 K

Space group	Pnma	
Lattice parameter (Å)	a=5.73509(10), b=7.41357(11), c=5.31189(8)	
Atom	x, y, z	Occupancy
Tb/Mn/Cu1	0.0790(3), 0.2500, 0.9839(2)	0.861/0.081/0.040
Mn/Cu2	0.0000, 0.0000, 0.5000	0.990/0.010
O1	0.4675(3), 0.2500, 0.1056(3)	1.000
O2	0.3196(3), 0.0504(3), 0.7043(3)	1.000
Phase 2		
Space group	$I4_1/amd$	
Lattice parameter (Å)	a=5.75859(9), c=9.43074(8)	
Atom	x, y, z	Occupancy
Mn/Tb/Cu[b]	0.0000, 0.2500, 0.8750	0.975/0.005/0.02
Mn/Tb/Cu	0.0000, 0.5000, 0.5000	0.975/0.005/0.02
O	0.0000, 0.4746, 0.2637	1.00
Phase 3 (magnetic only)	P1	
Lattice parameter (Å)	$a\approx b\approx c\approx 6.0115$, $\alpha\approx\beta\approx\gamma\approx 60^o$	
Atom	x, y, z	Mx, My, Mz
Mn1	0.0000, 0.0000, 0.0000	-1.423, 0.0000, 2.561
Mn2	0.5000, 0.0000, 0.0000	-1.423,0.0000, 2.561
Mn3	0.6250, 0.6250, 0.6250	1.423, 0.0000, -2.561
Mn4	0.3750, 0.3750, 0.3750	1.423, 0.0000, -2.561
Mn5	0.0000, 0.5000, 0.0000	-1.423, 0.0000, 2.561
Mn6	0.0000, 0.0000, 0.5000	-1.423, 0.0000, 2.561
R factor[a]	R_{wp}=0.037, R_p=0.027	

[a] R_p is sum($|I_0-I_C|$)/sum(I_0), and R_{wp} is weighted R factors for neutron diffraction data.

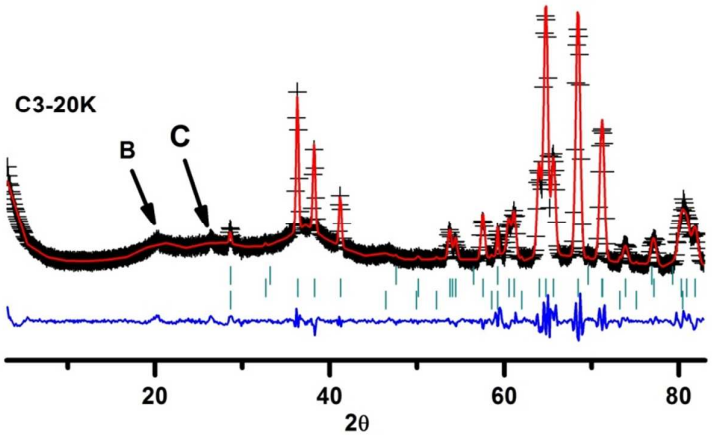

Figure S13a Rietveld plots of powder neutron diffraction patterns (λ=2.4270 Å) for C3 at 20 K. The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (middle one), nuclear (lower one) and magnetic (upper one) phase of $Mn_{1-x-y}Tb_xCu_yO_4$, and the difference curve is shown at the bottom of the figure. B, magnetic reflection of ICAM (incommensurate canted antiferromagnetic) ordering of Mn with a wave vector q_{Mn}= (~0.283, 0, 0) in the space group $Pna2_1$ setting. C, magnetic reflection of the CAM (canted antiferromagnetic) ordering of both Tb and Mn in the magnetic space group $Pn'a2_1'$. B and C are not refined.

Table S7a Rietveld refinement details of the neutron diffraction data for C3 at 20 K using GSAS

Space group	$Pna2_1$	
Lattice parameter (Å)	a=5.73225(10), b=5.31205(11), c=7.41459(8)	
Atom	x, y, z	Occupancy
Tb/Mn/Cu1	0.0782(3), 0.9889, 0.2571(2)	0.861/0.081/0.040
Mn/Cu2	0.0000, 0.5000, 0.0000	0.990/0.010
O1	0.4658(3), 0.1079(2), 0.2591(3)	1.000
O2	0.3284(3), 0.6886(3), 0.0821(3)	1.000
O3	0.1881(2), 0.2242(3), -0.0093(2)	1.000
Nuclear phase of $Mn_{1-x-y}Tb_xCu_yO_4$		
Space group	$I4_1/amd$	
Lattice parameter (Å)	a=5.75814(9), c=9.43245(8)	
Atom	x, y, z	Occupancy
Mn/Tb/Cu[b]	0.0000, 0.2500, 0.8750	0.95/0.02/0.03
Mn/Tb/Cu	0.0000, 0.5000, 0.5000	0.95/0.02/0.03
O	0.0000, 0.4746, 0.2637	1.00
Magnetic phase of $Mn_{1-x-y}Tb_xCu_yO_4$		
Space group	P1	
Lattice parameter (Å)	a≈b≈c≈6.0201, α≈β≈γ≈60°	
Atom	x, y, z	Mx, My, Mz
Mn1	0.0000, 0.0000, 0.0000	2.664, 0.0000, 4.381
Mn2	0.5000, 0.0000, 0.0000	2.664, 0.0000, 4.381
Mn3	0.6250, 0.6250, 0.6250	-2.664, 0.0000, -4.381
Mn4	0.3750, 0.3750, 0.3750	-2.664, 0.0000, -4.381
Mn5	0.0000, 0.5000, 0.0000	2.664, 0.0000, 4.381
Mn6	0.0000, 0.0000, 0.5000	2.664, 0.0000, 4.381
R factor[a]	R_{wp}=0.041, R_p=0.029	

[a]R_p is sum($|I_0-I_C|$)/sum(I_0), and R_{wp} is weighted R factors for neutron diffraction data.

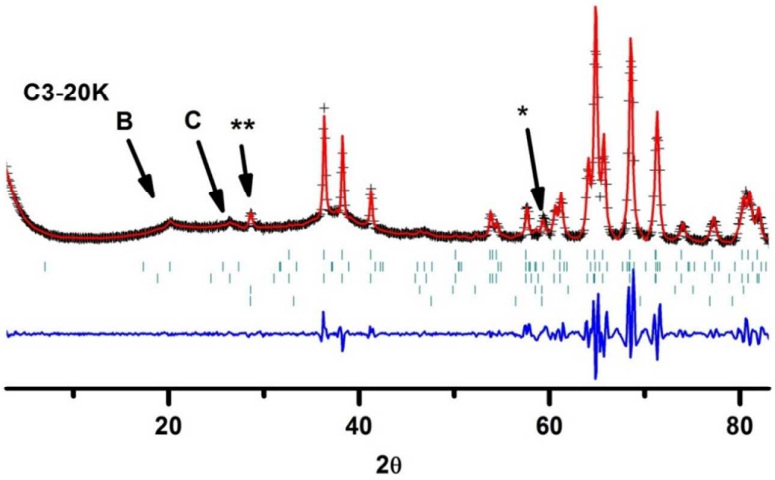

Figure S13b Rietveld plots of powder neutron diffraction patterns (λ=2.4270 Å) for C3 at 20 K. The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for nuclear phase of $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (the first line), nuclear (the fourth line) and magnetic (the fifth line) phase of $Mn_{1-x-y}Tb_xCu_yO_4$, and the difference curve is shown at the bottom of the figure. B, magnetic reflection of ICAM (incommensurate canted antiferromagnetic) ordering of Mn with a wave vector q_{Mn}= (~0.283, 0, 0) in the space group $Pna2_1$ setting. C, magnetic reflection of the CAM (canted antiferromagnetic) ordering of both Tb and Mn in the magnetic space group $Pn'a2_1'$.

Table S7b Rietveld refinement details of the neutron diffraction data for C3 collected at 20 K using Fullprof.

Nuclear Phase for C3		
Space group (nuclear phase)	$Pna2_1$	
Lattice parameter (Å)	a=5.73225(10), b=5.31205(11), c=7.41459(8)	
Atom	x, y, z	
Tb/Mn/Cu1[a]	0.0782(3), 0.9889, 0.2571(2)	
Mn/cu2[b]	0.0000, 0.5000, 0.0000	
O1	0.4658(3), 0.1079(2), 0.2591(3)	
O2	0.3284(3), 0.6886(3), 0.0821(3)	
O3	0.1881(2), 0.2242(3), -0.0093(2)	
Magnetic Phase B		
Space group	P1	
Lattice parameter (Å)	*a*=5.73225(10), *b*=5.31205(10), *c*=7.41459(10), α=β=γ=90°	
Atom	(x,y,z)/(Mx,My,Mz)	
Mn2a	(0.0000, 0.5000, 0.0000)/ (-1.71(3), 0.00, 0.00)	
Mn2b	(0.0000, 0.5000, 0.5000)/ (1.71(3), 0.00, 0.00)	
Mn2c	(0.5000, 0.0000, 0.0000)/(-1.71(3),0.00, 0.00)	
Mn2d	(0.5000, 0.0000, 0.5000)/ (1.71(3), 0.00, 0.00)	
q	(0.289(3), 0.000, 0.000)	
Magnetic Phase C		
Space group	*P1*	
Lattice parameter (Å)	*a*=5.73225(10), *b*=5.31205(10), *c*=7.41459(10), α=β=γ=90°	
Atom	(x,y,z)/(Mx,My,Mz)	
Mn2a	(0.0000, 0.5000, 0.0000)/ (0.24(3), -1.33(3), -0.03(3))	
Mn2b	(0.0000, 0.5000, 0.5000)/ (0.24(3), -1.33(3), 0.03(3))	
Mn2c	(0.5000, 0.0000, 0.0000)/(-0.24(3), -1.33(3), -0.03(3))	
Mn2d	(0.5000, 0.0000, 0.5000)/ (-0.24(3), -1.33(3), 0.03(3))	
Mn/Tb1a	(0.0782(3), 0.9889(1), 0.2571(1))/ (0.11(3), 1.49(3), 0.03(3))	
Mn/Tb1b	(0.9218(2), 0.0111(3), -0.24291))/ (0.11(3), 1.49(3), -0.03(3))	
Mn/Tb1c	(0.4218(1), 0.5111(1), -0.2429(1))/(-0.11(3), 1.49(3), 0.03(3))	
Mn/Tb1d	(0.5782(1), 0.4889(1), 0.2571(1))/ (-0.11(3), 1.49(3), -0.03(3))	
Nuclear phase of $Mn_{1-x-y}Tb_xCu_yO_4$		
Space group	$I4_1/amd$	
Lattice parameter (Å)	a=5.75814(9), c=9.43245(8)	
Atom	x, y, z	Occupancy
Mn/Tb/Cu[b]	0.0000, 0.2500, 0.8750	0.975/0.005/0.02
Mn/Tb/Cu	0.0000, 0.5000, 0.5000	0.975/0.005/0.02
O	0.0000, 0.4746, 0.2637	1.00
Magnetic phase of $Mn_{1-x-y}Tb_xCu_yO_4$		
Space group	P1	
Lattice parameter (Å)	$a\approx b\approx c\approx 6.0201$, $\alpha\approx\beta\approx\gamma\approx 60^o$	
Atom	x, y, z	Mx, My, Mz
Mn1	0.0000, 0.0000, 0.0000	2.664, 0.0000, 4.381
Mn2	0.5000, 0.0000, 0.0000	2.664, 0.0000, 4.381
Mn3	0.6250, 0.6250, 0.6250	-2.664, 0.0000, -4.3813
Mn4	0.3750, 0.3750, 0.3750	-2.664, 0.0000, -4.381
Mn5	0.0000, 0.5000, 0.0000	2.664, 0.0000, 4.381
Mn6	0.0000, 0.0000, 0.5000	2.664, 0.0000, 4.381
R factor[b]	R_B^1=0.053, R_F^1=0.024; R^{MB}=0.065; R^{MC}=0.034; R_B^2=0.105, R_F^2=0.056; R^M=0.060	

[a]The occupancy of Tb1/Mn1/Cu1 is 0.861/0.081/0.040.

[b]The occupancy of Mn/Cu2 is 0.940/0.060.

[c]R_B^1, R_F^1, R^{MB}, R^{MC}, R_B^2, R_F^2 and R^M are the Bragg R-factor and RF-factor of C3, Magnetic R-factor for magnetic phase B and C, the Bragg R-factor and R-factor for $Mn_{1-x-y}Tb_xCu_yO_4$, and Magnetic R-factor for $Mn_{1-x-y}Tb_xCu_yO_4$.

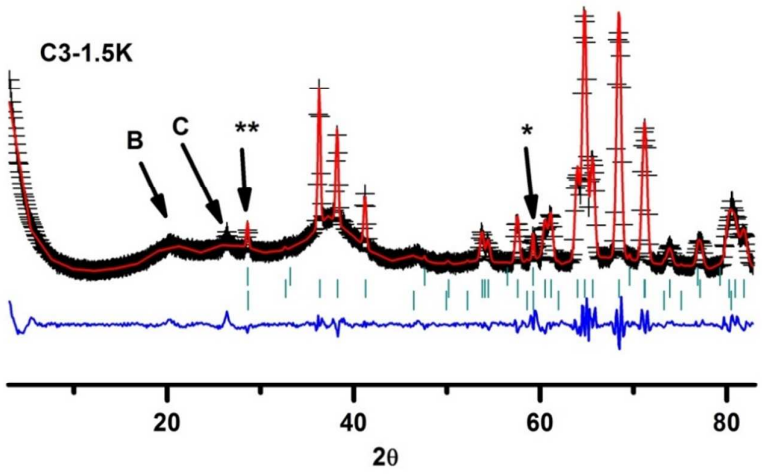

Figure S14a Rietveld plots of powder neutron diffraction patterns (λ=2.4270 Å) for C3 at 1.5 K. The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (middle one), nuclear (lower one) and magnetic (upper one) phase of $Mn_{1-x-y}Tb_xCu_yO_4$, and the difference curve is shown at the bottom of the figure. B, magnetic reflection of ICAM (incommensurate canted antiferromagnetic) ordering of Mn with a wave vector q_{Mn}= (~0.283, 0, 0) in the space group $Pna2_1$ setting. C, magnetic reflection of the CAM (canted antiferromagnetic) ordering of both Tb and Mn in the magnetic space group $Pn'a2_1'$. B and C are not refined.

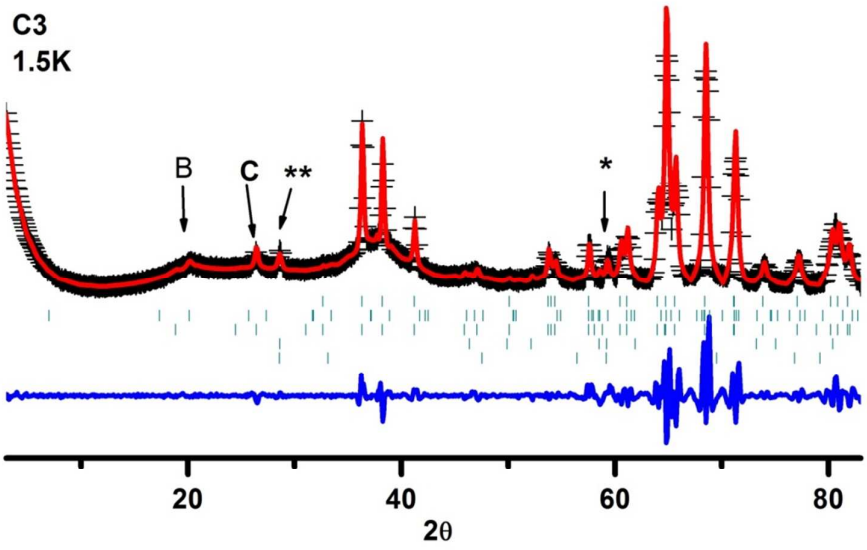

Figure S14b Rietveld plots of powder neutron diffraction patterns (λ=2.4270 Å) for C3 at 1.5 K. The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for nuclear phase of $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (the first line), nuclear (the fourth line) and magnetic (the fifth line) phase of $Mn_{1-x-y}Tb_xCu_yO_4$, and the difference curve is shown at the bottom of the figure. B, magnetic reflection of ICAM (incommensurate canted antiferromagnetic) ordering of Mn with a wave vector q_{Mn}= (~0.283, 0, 0) in the space group $Pna2_1$ setting. C, magnetic reflection of the CAM (canted antiferromagnetic) ordering of both Tb and Mn in the magnetic space group $Pn'a2_1'$.

Table S8a Rietveld refinement details of the neutron diffraction data for C3 at 1.5 K using GSAS

Space group	$Pna2_1$	
Lattice parameter (Å)	a=5.73137(10), b=5.31223(11), c=7.41493(8)	
Atom	x, y, z	Occupancy
Tb/Mn/Cu1	0.0781(3), 0.9894, 0.2585(2)	0.861/0.081/0.040
Mn/Cu2	0.0000, 0.5000, 0.0000	0.990/0.010
O1	0.4654(3), 0.1081(2), 0.2606(3)	1.000
O2	0.3333(3), 0.6912(3), 0.0864(3)	1.000
O3	0.1912(2), 0.2208(3), -0.0064(2)	1.000
Nuclear phase of $Mn_{1-x-y}Tb_xCu_yO_4$		
Space group	$I4_1/amd$	
Lattice parameter (Å)	a=5.75517(9), c=9.44091(8)	
Atom	x, y, z	Occupancy
Mn/Tb/Cu[b]	0.0000, 0.2500, 0.8750	0.975/0.005/0.02
Mn/Tb/Cu	0.0000, 0.5000, 0.5000	0.975/0.005/0.02
O	0.0000, 0.4746, 0.2637	1.00
Magnetic phase of $Mn_{1-x-y}Tb_xCu_yO_4$		
Space group	P1	
Lattice parameter (Å)	$a\approx b\approx c\approx 6.0203$, $\alpha\approx\beta\approx\gamma\approx 60^o$	
Atom	x, y, z	Mx, My, Mz
Mn1	0.0000, 0.0000, 0.0000	1.241, 0.0000, 4.839
Mn2	0.5000, 0.0000, 0.0000	1.241, 0.0000, 4.839
Mn3	0.6250, 0.6250, 0.6250	-1.241, 0.0000, -4.839
Mn4	0.3750, 0.3750, 0.3750	-1.241, 0.0000,- 4.839
Mn5	0.0000, 0.5000, 0.0000	1.241, 0.0000, 4.839
Mn6	0.0000, 0.0000, 0.5000	1.241, 0.0000, 4.839
R factor[a]	R_{wp}=0.044, R_p=0.032	

[a] R_p is sum($|I_0-I_C|$)/sum(I_0), and R_{wp} is weighted R factors for neutron diffraction data.

Table S8b Rietveld refinement details of the neutron diffraction data for C3 collected at 1.5 K using Fullprof.

Nuclear Phase for C3		
Space group (nuclear phase)	$Pna2_1$	
Lattice parameter (Å)	a=5.73137(10), b=5.31223(11), c=7.41493(8)	
Atom	x, y, z	Occupancy
Tb/Mn/Cu1[a]	0.0781(3), 0.9894, 0.2585(2)	0.861/0.081/0.040
Mn/cu2[b]	0.0000, 0.5000, 0.0000	0.990/0.010
O1	0.4654(3), 0.1081(2), 0.2606(3)	1.000
O2	0.3333(3), 0.6912(3), 0.0864(3)	1.000
O3	0.1912(2), 0.2208(3), -0.0064(2)	1.000
Magnetic Phase B		
Space group	P1	
Lattice parameter (Å)	a=5.73137(10), b=5.31223(11), c=7.41493(8), α=β=γ=90°	
Atom	(x,y,z)/(Mx,My,Mz)	
Mn2a	(0.0000, 0.5000, 0.0000)/ (-1.91(3), 0.00, 0.00)	
Mn2b	(0.0000, 0.5000, 0.5000)/ (1.91(3), 0.00, 0.00)	
Mn2c	(0.5000, 0.0000, 0.0000)/(-1.91(3),0.00, 0.00)	
Mn2d	(0.5000, 0.0000, 0.5000)/ (1.91(3), 0.00, 0.00)	
q	(0.289(3), 0.000, 0.000)	
Magnetic Phase C		
Space group	*P1*	
Lattice parameter (Å)	a=5.73137(10), b=5.31223(11), c=7.41493(8), α=β=γ=90°	
Atom	(x,y,z)/(Mx,My,Mz)	
Mn2a	(0.0000, 0.5000, 0.0000)/ (1.44(3), -1.43(3), -0.03(3))	
Mn2b	(0.0000, 0.5000, 0.5000)/ (1.44(3), -1.43(3), 0.03(3))	
Mn2c	(0.5000, 0.0000, 0.0000)/(-1.44(3), -1.43(3), -0.03(3))	
Mn2d	(0.5000, 0.0000, 0.5000)/ (-1.44(3), -1.43(3), 0.03(3))	
Mn/Tb1a	(0.0781(3), 0.9894(1), 0.2585(1))/ (0.11(3), 1.49(3), 0.03(3))	
Mn/Tb1b	(0.9219(2), 0.0106(3), -0.2415(1))/ (0.11(3), 1.49(3), -0.03(3))	
Mn/Tb1c	(0.4219(1), 0.5106(1), -0.2415(1))/(-0.11(3), 1.49(3), 0.03(3))	
Mn/Tb1d	(0.5781(1), 0.4894(1), 0.2585(1))/ (-0.11(3), 1.49(3), -0.03(3))	
Nuclear phase of $Mn_{1-x-y}Tb_xCu_yO_4$		
Space group	$I4_1/amd$	
Lattice parameter (Å)	a=5.75517(9), c=9.44091(8)	
Atom	x, y, z	Occupancy
Mn/Tb/Cu[b]	0.0000, 0.2500, 0.8750	0.975/0.005/0.02
Mn/Tb/Cu	0.0000, 0.5000, 0.5000	0.975/0.005/0.02
O	0.0000, 0.4746, 0.2637	1.00
Magnetic phase of $Mn_{1-x-y}Tb_xCu_yO_4$		
Space group	P1	
Lattice parameter (Å)	a≈b≈c≈6.0203, α≈β≈γ≈60°	
Atom	x, y, z	Mx, My, Mz
Mn1	0.0000, 0.0000, 0.0000	1.241, 0.0000, 4.839
Mn2	0.5000, 0.0000, 0.0000	1.241, 0.0000, 4.839
Mn3	0.6250, 0.6250, 0.6250	-1.241, 0.0000, -4.839
Mn4	0.3750, 0.3750, 0.3750	-1.241, 0.0000,- 4.839
Mn5	0.0000, 0.5000, 0.0000	1.241, 0.0000, 4.839
Mn6	0.0000, 0.0000, 0.5000	1.241, 0.0000, 4.839
R factor[c]	R_B^1=0.057, R_F^1=0.026; R^{MB}=0.053; R^{MC}=0.037; R_B^2=0.111, R_F^2=0.075; R^M=0.053	

[a]The occupancy of Tb1/Mn1/Cu1 is 0.861/0.081/0.040.

[b]The occupancy of Mn/Cu2 is 0.940/0.060.

[c]R_B^1, R_F^1, R^{MB}, R^{MC}, R_B^2, R_F^2 and R^M are the Bragg R-factor and RF-factor of C3, Magnetic R-factor for magnetic phase B and C, the Bragg R-factor and R-factor for $Mn_{1-x-y}Tb_xCu_yO_4$, and Magnetic R-factor for $Mn_{1-x-y}Tb_xCu_yO_4$.

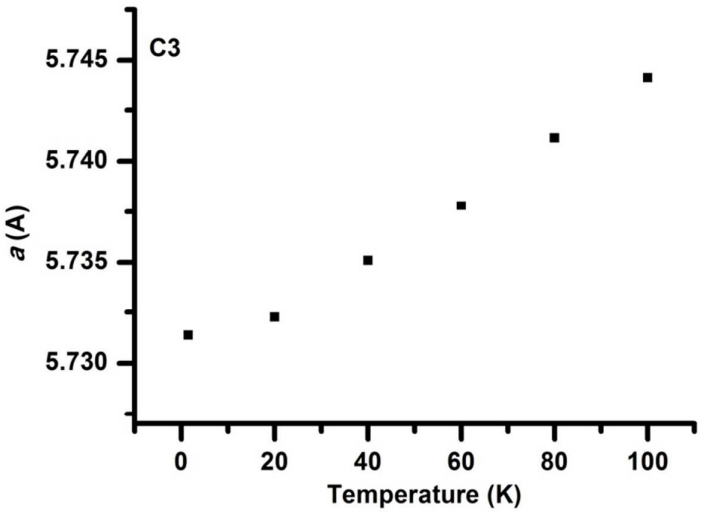

Figure S15 Temperature dependent lattice parameter *a* of C3.

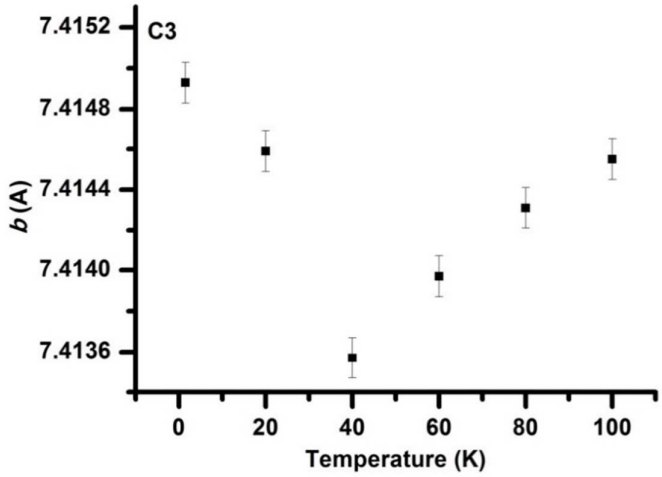

Figure S16 Temperature dependent lattice parameter *b* of C3 (in Pnma setting for temperature is above 40 K) or *c* of C3 (in Pna21 setting for temperature is below 40 K).

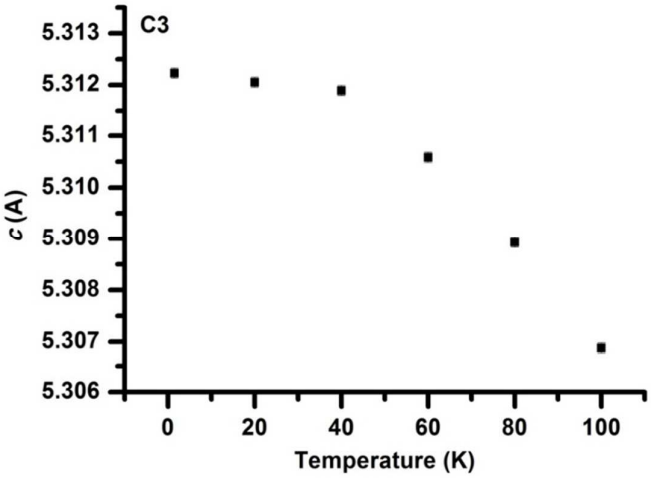

Figure S17 Temperature dependent lattice parameter *c* of C3 (in *Pnma* setting for temperature is above 40K) or *b* of C3 (in $Pna2_1$ setting for temperature is below 40K).

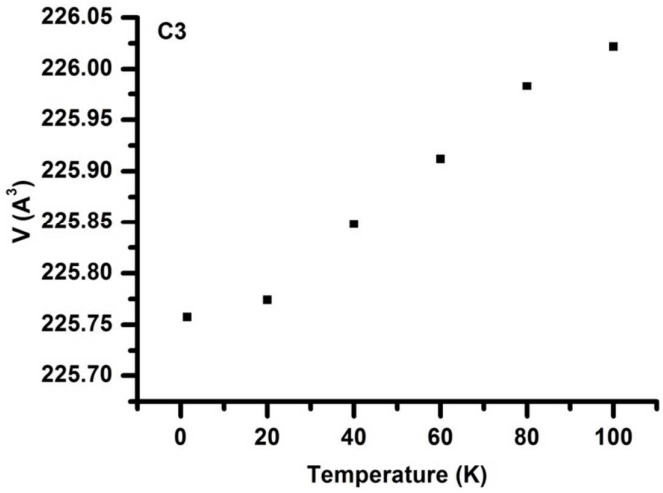

Figure S18 Temperature dependent unit cell volume V of C3.

5. The refinement details of the neutron diffraction data for C5 at selected temperature

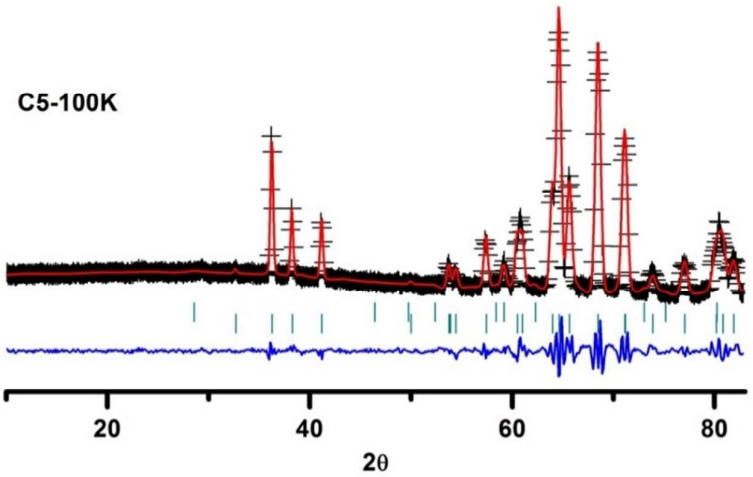

Figure S19 Rietveld plots of powder neutron diffraction patterns (λ=2.4270 Å) for C5 at 100K. The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (lower one), $Mn_{1-x-y}Tb_xCu_yO_4$ (upper one), and the difference curve is shown at the bottom of the figure.

Table S9 Rietveld refinement details of the neutron diffraction data for C5 at 100K

Space group	Pnma	
Lattice parameter (Å)	a=5.74180(8), b=7.40354(9), c=5.30484(7)	
Atom	x, y, z	Occupancy
Tb/Mn/Cu1	0.0778(3), 0.2500, 0.9828(2)	0.861/0.081/0.040
Mn/Cu2	0.0000, 0.0000, 0.5000	0.940/0.060
O1	0.4583(3), 0.2500, 0.1007(3)	1.000
O2	0.3214(3), 0.0531(3), 0.7037(3)	1.000
Phase 2		
Space group	$I\,4_1/amd$	
Lattice parameter (Å)	a=5.76663(8), c=9.38045(9)	
Atom	x, y, z	Occupancy
Mn/Tb/Cu	0.0000, 0.2500, 0.8750	0.975/0.005/0.02
Mn/Tb/Cu	0.0000, 0.5000, 0.5000	0.975/0.005/0.02
O	0.0000, 0.4746, 0.2637	1.000
R factor[a]	R_{wp}=0.044, R_p=0.029	

[a] R_p is sum($|I_0-I_C|$)/sum(I_0), and R_{wp} is weighted R factors for neutron diffraction data.

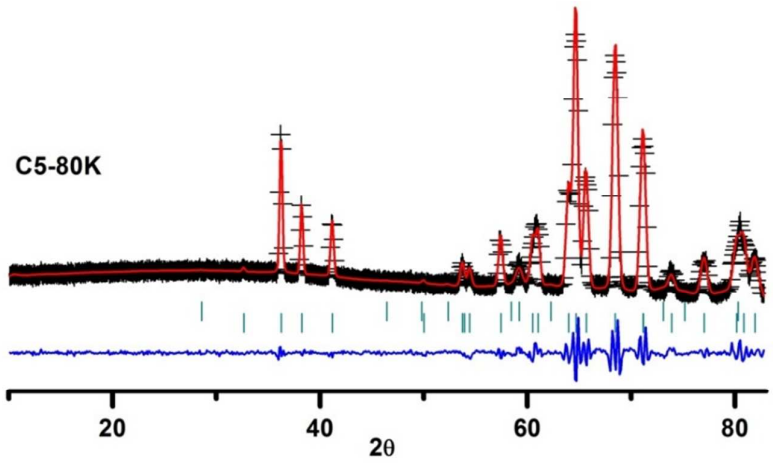

Figure S20 Rietveld plots of powder neutron diffraction patterns (λ=2.4270 Å) for C5 at 80K. The The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (lower one), $Mn_{1-x-y}Tb_xCu_yO_4$ (upper one), and the difference curve is shown at the bottom of the figure.

Table S10 Rietveld refinement details of the neutron diffraction data for C5 at 80K

Space group	Pnma	
Lattice parameter (Å)	a=5.73904(8), b=7.40226(9), c=5.30583(7)	
Atom	x, y, z	Occupancy
Tb/Mn/Cu1	0.0753(3), 0.2500, 0.9832(2)	0.861/0.081/0.040
Mn/Cu2	0.0000, 0.0000, 0.5000	0.940/0.060
O1	0.4582(3), 0.2500, 0.1037(3)	1.000
O2	0.3200(3), 0.0545(3), 0.7044(3)	1.000
Phase 2		
Space group	$I4_1/amd$	
Lattice parameter (Å)	a=5.76358(7), c=9.38221(9)	
Atom	x, y, z	Occupancy
Mn/Tb/Cu	0.0000, 0.2500, 0.8750	0.975/0.005/0.02
Mn/Tb/Cu	0.0000, 0.5000, 0.5000	0.975/0.005/0.02
O	0.0000, 0.4746, 0.2637	1.000
R factor[a]	R_{wp}=0.040, R_p=0.026	

[a]R_p is sum($|I_0-I_C|$)/sum(I_0), and R_{wp} is weighted R factors for neutron diffraction data.

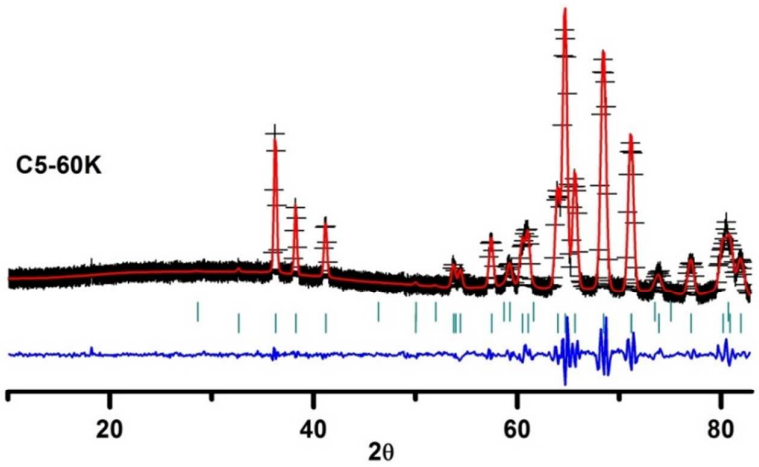

Figure S21 Rietveld plots of powder neutron diffraction patterns (λ=2.4270 Å) for C5 at 60K. The The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (lower one), $Mn_{1-x-y}Tb_xCu_yO_4$ (upper one), and the difference curve is shown at the bottom of the figure.

Table S11 Rietveld refinement details of the neutron diffraction data for C5 at 60K

Space group	Pnma	
Lattice parameter (Å)	a=5.73634(8), b=7.40141(9), c=5.30728(7)	
Atom	x, y, z	Occupancy
Tb/Mn/Cu1	0.0750(3), 0.2500, 0.9835(2)	0.861/0.081/0.040
Mn/Cu2	0.0000, 0.0000, 0.5000	0.940/0.060
O1	0.4590(3), 0.2500, 0.1046(3)	1.000
O2	0.3198(3), 0.0543(3), 0.7042(3)	1.000
Phase 2		
Space group	$I4_1/amd$	
Lattice parameter (Å)	a=5.73521(7), c=9.47832(9)	
Atom	x, y, z	Occupancy
Mn/Tb/Cu	0.0000, 0.2500, 0.8750	0.975/0.005/0.02
Mn/Tb/Cu	0.0000, 0.5000, 0.5000	0.975/0.005/0.02
O	0.0000, 0.4746, 0.2637	1.000
R factor[a]	R_{wp}=0.041, R_p=0.027	

[a] R_p is sum($|I_0-I_C|$)/sum(I_0), and R_{wp} is weighted R factors for neutron diffraction data.

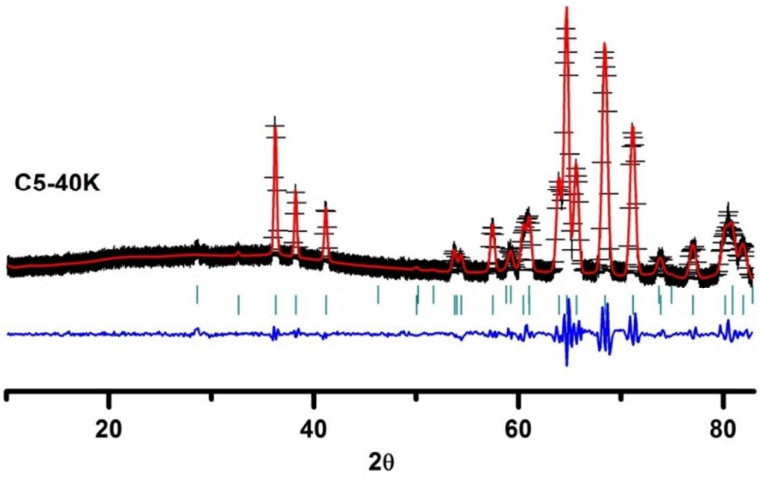

Figure S22 Rietveld plots of powder neutron diffraction patterns (λ=2.4270 Å) for C5 at 40K. The The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (lower one), $Mn_{1-x-y}Tb_xCu_yO_4$ (upper one), and the difference curve is shown at the bottom of the figure.

Table S12 Rietveld refinement details of the neutron diffraction data for C5 at 40K

Space group	Pnma	
Lattice parameter (Å)	a=5.73404(8), b=7.40167(9), c=5.30928(7)	
Atom	x, y, z	Occupancy
Tb/Mn/Cu1	0.0749(3), 0.2500, 0.9836(2)	0.861/0.081/0.040
Mn/Cu2	0.0000, 0.0000, 0.5000	0.940/0.060
O1	0.4580(3), 0.2500, 0.1039(3)	1.000
O2	0.3202(3), 0.0546(3), 0.7046(3)	1.000
Phase 2		
Space group	$I4_1/amd$	
Lattice parameter (Å)	a=5.72064(7), c=9.55427(9)	
Atom	x, y, z	Occupancy
Mn/Tb/Cu	0.0000, 0.2500, 0.8750	0.975/0.005/0.02
Mn/Tb/Cu	0.0000, 0.5000, 0.5000	0.975/0.005/0.02
O	0.0000, 0.4746, 0.2637	1.000
R factor[a]	R_{wp}=0.042, R_p=0.028	

[a] R_p is sum($|I_0-I_C|$)/sum(I_0), and R_{wp} is weighted R factors for neutron diffraction data.

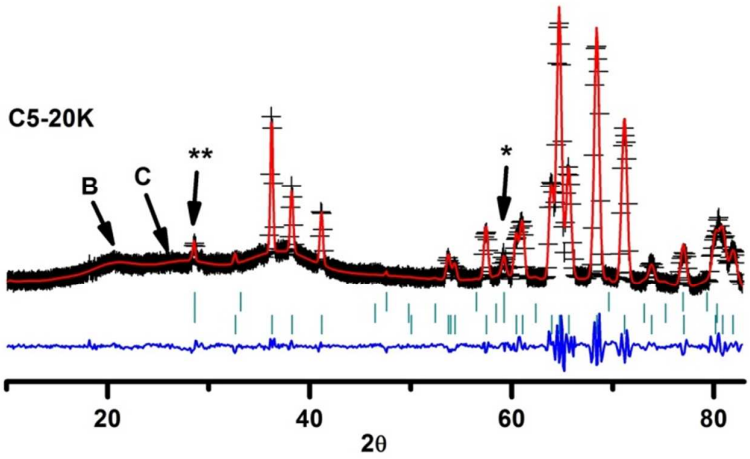

Figure S23a Rietveld plots of powder neutron diffraction patterns (λ=2.4270 Å) for C5 at 20K. The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (middle one), nuclear (lower one) and magnetic (upper one) phase of $Mn_{1-x-y}Tb_xCu_yO_4$, and the difference curve is shown at the bottom of the figure. B, magnetic reflection of ICAM (incommensurate canted antiferromagnetic) ordering of Mn with a wave vector q_{Mn}= (~0.283, 0, 0) in the space group *Pna2₁* setting. C, magnetic reflection of the CAM (canted antiferromagnetic) ordering of both Tb and Mn in the magnetic space group *Pn'a2₁'*. B and C are not refined.

Table S13a Rietveld refinement details of the neutron diffraction data for C5 at 20 K using GSAS

Space group	$Pna2_1$	
Lattice parameter (Å)	a=5.73381(8), b=5.31016(7), c=7.40447(9)	
Atom	x, y, z	Occupancy
Tb/Mn/Cu1	0.0642(3), 0.9824, 0.2412(2)	0.861/0.081/0.040
Mn/Cu2	0.0000, 0.5000, 0.0000	0.940/0.060
O1	0.4542(3), 0.0998, 0.1982(3)	1.000
O2	0.3021(3), 0.6941(3), 0.0370(3)	1.000
O3	0.1562(3), 0.2210(3), -0.0655(2)	1.000
Nuclear phase of $Mn_{1-x-y}Tb_xCu_yO_4$		
Space group	$I4_1/amd$	
Lattice parameter (Å)	a=5.76123(7), c=9.37174(9)	
Atom	x, y, z	Occupancy
Mn/Tb/Cu	0.0000, 0.2500, 0.8750	0.975/0.005/0.02
Mn/Tb/Cu	0.0000, 0.5000, 0.5000	0.975/0.005/0.02
O	0.0000, 0.4746, 0.2637	1.000
Magnetic phase of $Mn_{1-x-y}Tb_xCu_yO_4$		
Space group	P1	
Lattice parameter (Å)	$a\approx b\approx c\approx 6.0106$, $\alpha\approx\beta\approx\gamma\approx 60^o$	
Atom	x, y, z	Mx, My, Mz
Mn1	0.0000, 0.0000, 0.0000	2.440, -1.000, 2.100
Mn2	0.5000, 0.0000, 0.0000	2.440, -1.000, 2.100
Mn3	0.6250, 0.6250, 0.6250	-2.440, 1.000, -2.100
Mn4	0.3750, 0.3750, 0.3750	-2.440, 1.000, -2.100
Mn5	0.0000, 0.5000, 0.0000	2.440, -1.000, 2.100
Mn6	0.0000, 0.0000, 0.5000	2.440, -1.000, 2.100
R factor[a]	R_{wp}=0.044, R_p=0.029	

[a] R_p is sum($|I_0-I_C|$)/sum(I_0), and R_{wp} is weighted R factors for neutron diffraction data.

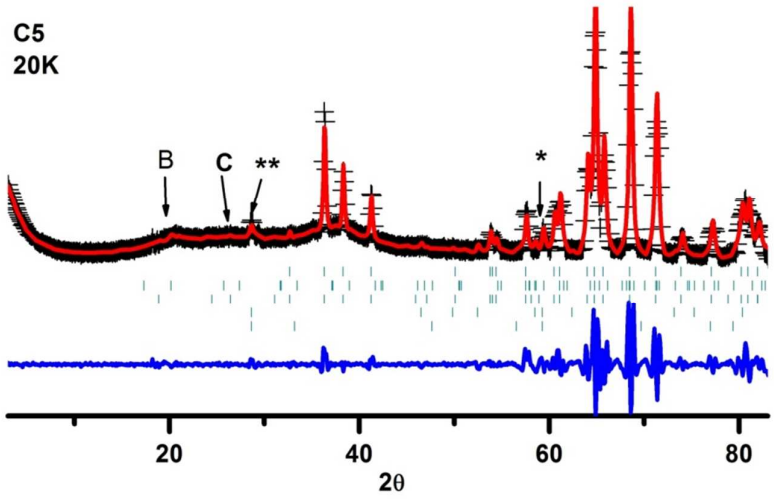

Figure S23b Rietveld plots of powder neutron diffraction patterns (λ=2.4270 Å) for C5 at 20K. The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for nuclear phase of $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (the first line), nuclear (the fourth line) and magnetic (the fifth line) phase of $Mn_{1-x-y}Tb_xCu_yO_4$, and the difference curve is shown at the bottom of the figure. B, magnetic reflection of ICAM (incommensurate canted antiferromagnetic) ordering of Mn with a wave vector q_{Mn}= (~0.283, 0, 0) in the space group $Pna2_1$ setting. C, magnetic reflection of the CAM (canted antiferromagnetic) ordering of both Tb and Mn in the magnetic space group $Pn'a2_1'$.

Table S13b Rietveld refinement details of the neutron diffraction data for C5 at 20K using Fullprof

Space group	$Pna2_1$	
Lattice parameter (Å)	a=5.73381(8), b=5.31016(7), c=7.40447(9)	
Atom	x, y, z	Occupancy
Tb/Mn/Cu1	0.0642(3), 0.9824, 0.2412(2)	0.861/0.081/0.040
Mn/Cu2	0.0000, 0.5000, 0.0000	0.940/0.060
O1	0.4542(3), 0.0998, 0.1982(3)	1.000
O2	0.3021(3), 0.6941(3), 0.0370(3)	1.000
O3	0.1562(3), 0.2210(3), -0.0655(2)	1.000
Nuclear phase of $Mn_{1-x-y}Tb_xCu_yO_4$		
Space group	$I4_1/amd$	
Lattice parameter (Å)	a=5.76123(7), c=9.37174(9)	
Atom	x, y, z	Occupancy
Mn/Tb/Cu	0.0000, 0.2500, 0.8750	0.9750/0.005/0.020
Mn/Tb/Cu	0.0000, 0.5000, 0.5000	0.9750/0.005/0.020
O	0.0000, 0.4746, 0.2637	1.000
Magnetic phase of $Mn_{1-x-y}Tb_xCu_yO_4$		
Space group	P1	
Lattice parameter (Å)	$a\approx b\approx c\approx 6.0106$, $\alpha\approx\beta\approx\gamma\approx 60^o$	
Atom	x, y, z	Mx, My, Mz
Mn1	0.0000, 0.0000, 0.0000	2.440, -1.000, 2.100
Mn2	0.5000, 0.0000, 0.0000	2.440, -1.000, 2.100
Mn3	0.6250, 0.6250, 0.6250	-2.440, 1.000, -2.100
Mn4	0.3750, 0.3750, 0.3750	-2.440, 1.000, -2.100
Mn5	0.0000, 0.5000, 0.0000	2.440, -1.000, 2.100
Mn6	0.0000, 0.0000, 0.5000	2.440, -1.000, 2.100

Magnetic Phase B	
Space group	P1
Lattice parameter (Å)	a=5.73137(10), b=5.31223(11), c=7.41493(8), $\alpha=\beta=\gamma=90°$
Atom	(x,y,z)/(Mx,My,Mz)
Mn2a	(0.0000, 0.5000, 0.0000)/ (-1.51(3), 0.00, 0.00)
Mn2b	(0.0000, 0.5000, 0.5000)/ (1.51(3), 0.00, 0.00)
Mn2c	(0.5000, 0.0000, 0.0000)/(-1.51(3),0.00, 0.00)
Mn2d	(0.5000, 0.0000, 0.5000)/ (1.51(3), 0.00, 0.00)
q	(0.289(3), 0.000, 0.000)
Magnetic Phase C	
Space group	*P1*
Lattice parameter (Å)	a=5.73137(10), b=5.31223(11), c=7.41493(8), $\alpha=\beta=\gamma=90°$
Atom	(x,y,z)/(Mx,My,Mz)
Mn2a	(0.0000, 0.5000, 0.0000)/ (0.44(3), -1.03(3), -0.03(3))
Mn2b	(0.0000, 0.5000, 0.5000)/ (0.44(3), -1.03(3), 0.03(3))
Mn2c	(0.5000, 0.0000, 0.0000)/(-0.44(3), -1.03(3), -0.03(3))
Mn2d	(0.5000, 0.0000, 0.5000)/ (-0.44(3), -1.03(3), 0.03(3))
Mn/Tb1a	(0.0781(3), 0.9894(1), 0.2585(1))/ (0.11(3), 0.89(3), 0.03(3))
Mn/Tb1b	(0.9219(2), 0.0106(3), -0.2415(1))/ (0.11(3), 0.89(3), -0.03(3))
Mn/Tb1c	(0.4219(1), 0.5106(1), -0.2415(1))/(-0.11(3), 0.89(3), 0.03(3))
Mn/Tb1d	(0.5781(1), 0.4894(1), 0.2585(1))/ (-0.11(3), 0.89(3), -0.03(3))
R factor[a]	R_B^1=0.053, R_F^1=0.028; R^{MB}=0.053; R^{MC}=0.039; R_B^2=0.088, R_F^2=0.090; R^M=0.159

[a] R_B^1, R_F^1, R^{MB}, R^{MC}, R_B^2, R_F^2 and R^M are the Bragg R-factor and RF-factor of C3, Magnetic R-factor for magnetic phase B and C, the Bragg R-factor and R-factor for $Mn_{1-x-y}Tb_xCu_yO_4$, and Magnetic R-factor for $Mn_{1-x-y}Tb_xCu_yO_4$.

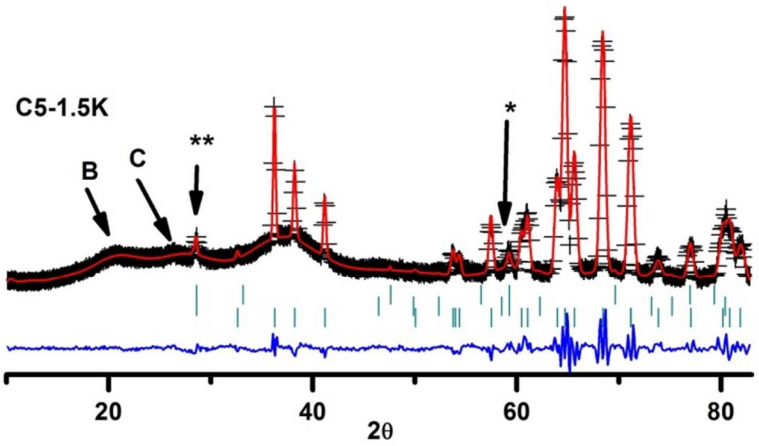

Figure S24a Rietveld plots of powder neutron diffraction patterns (λ=2.4270 Å) for C5 at 1.5K. The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (middle one), nuclear (lower one) and magnetic (upper one) phase of $Mn_{1-x-y}Tb_xCu_yO_4$, and the difference curve is shown at the bottom of the figure. B, magnetic reflection of ICAM (incommensurate canted antiferromagnetic) ordering of Mn with a wave vector q_{Mn}= (~0.283, 0, 0) in the space group $Pna2_1$ setting. C, magnetic reflection of the CAM (canted antiferromagnetic) ordering of both Tb and Mn in the magnetic space group $Pn'a2_1'$. B and C are not refined.

Table S14a Rietveld refinement details of the neutron diffraction data for C5 at 1.5 K using GSAS

Space group	$Pna2_1$	
Lattice parameter (Å)	a=5.73349(8), b=5.31052(7) , c=7.40571(9)	
Atom	x, y, z	Occupancy
Tb/Mn/Cu1	0.0784(3), 0.9849(3), 0.2564(2)	0.861/0.081/0.040
Mn/Cu2	0.0000, 0.5000, 0.0000	0.940/0.060
O1	0.4612(3), 0.1058, 0.2892(3)	1.000
O2	0.3088(3), 0.7136(3), 0.0573(3)	1.000
O3	0.1644(3), 0.2027(3), -0.0492(2)	1.000
Phase 2		
Space group	$I4_1/amd$	
Lattice parameter (Å)	a=5.75597(7), c=9.38882(9)	
Atom	x, y, z	Occupancy
Mn/Tb/Cu	0.0000, 0.2500, 0.8750	0.940/0.020/0.040
Mn/Tb/Cu	0.0000, 0.5000, 0.5000	0.940/0.020/0.040
O	0.0000, 0.4746, 0.2637	1.000
Magnetic phase of	$Mn_{1-x-y}Tb_xCu_yO_4$	
Space group	P1	
Lattice parameter (Å)	$a\approx b\approx c\approx 6.0103$, $\alpha\approx\beta\approx\gamma\approx 60^o$	
Atom	x, y, z	Mx, My, Mz
Mn1	0.0000, 0.0000, 0.0000	3.020, 0.900, 2.100
Mn2	0.5000, 0.0000, 0.0000	3.020, 0.900, 2.100
Mn3	0.6250, 0.6250, 0.6250	-3.020, -0.900, -2.100
Mn4	0.3750, 0.3750, 0.3750	-3.020, -0.900, -2.100
Mn5	0.0000, 0.5000, 0.0000	3.020, 0.900, 2.100
Mn6	0.0000, 0.0000, 0.5000	3.020, 0.900, 2.1000
R factor[a]	R_{wp}=0.048, R_p=0.033	

[a] R_p is sum($|I_0-I_C|$)/sum(I_0), and R_{wp} is weighted R factors for neutron diffraction data.

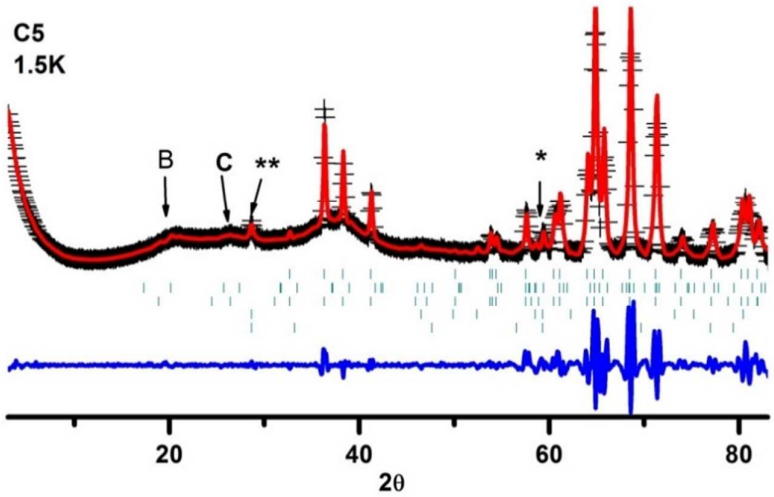

Figure S24b Rietveld plots of powder neutron diffraction patterns (λ=2.4270 Å) for C5 at 1.5 K. The symbol + represents the observed value, the solid line represents the calculated value; the marks below the diffraction patterns are the calculated reflection positions for nuclear phase of $Tb_{0.861}Mn_{0.121}Mn_{1-x}Cu_xO_{3-\delta}$ (the first line), nuclear (the fourth line) and magnetic (the fifth line) phase of $Mn_{1-x-y}Tb_xCu_yO_4$, and the difference curve is shown at the bottom of the figure. B, magnetic reflection of ICAM (incommensurate canted antiferromagnetic) ordering of Mn with a wave vector q_{Mn}= (~0.283, 0, 0) in the space group $Pna2_1$ setting. C, magnetic reflection of the CAM (canted antiferromagnetic) ordering of both Tb and Mn in the magnetic space group $Pn'a2_1'$.

Table S14b Rietveld refinement details of the neutron diffraction data for C5 at 1.5 K using Fullprof.

Space group	$Pna2_1$	
Lattice parameter (Å)	a=5.73349(8), b=5.31052(7) , c=7.40571(9)	
Atom	x, y, z	Occupancy
Tb/Mn/Cu1	0.0784(3), 0.9849(3), 0.2564(2)	0.861/0.081/0.040
Mn/Cu2	0.0000, 0.5000, 0.0000	0.940/0.060
O1	0.4612(3), 0.1058, 0.2892(3)	1.000
O2	0.3088(3), 0.7136(3), 0.0573(3)	1.000
O3	0.1644(3), 0.2027(3), -0.0492(2)	1.000
Phase 2		
Space group	$I4_1/amd$	
Lattice parameter (Å)	a=5.75597(7), c=9.38882(9)	
Atom	x, y, z	Occupancy
Mn/Tb/Cu	0.0000, 0.2500, 0.8750	0.940/0.020/0.040
Mn/Tb/Cu	0.0000, 0.5000, 0.5000	0.940/0.020/0.040
O	0.0000, 0.4746, 0.2637	1.000
Magnetic phase of	$Mn_{1-x-y}Tb_xCu_yO_4$	
Space group	P1	
Lattice parameter (Å)	$a\approx b\approx c\approx 6.0103$, $\alpha\approx\beta\approx\gamma\approx 60^o$	
Atom	x, y, z	Mx, My, Mz
Mn1	0.0000, 0.0000, 0.0000	3.020, 0.900, 2.100
Mn2	0.5000, 0.0000, 0.0000	3.020, 0.900, 2.100
Mn3	0.6250, 0.6250, 0.6250	-3.020, -0.900, -2.100
Mn4	0.3750, 0.3750, 0.3750	-3.020, -0.900, -2.100
Mn5	0.0000, 0.5000, 0.0000	3.020, 0.900, 2.100
Mn6	0.0000, 0.0000, 0.5000	3.020, 0.900, 2.1000

Magnetic Phase B		
Space group	P1	
Lattice parameter (Å)	a=5.73137(10), b=5.31223(11), c=7.41493(8), α=β=γ=90°	
Atom	(x,y,z)/(Mx,My,Mz)	
Mn2a	(0.0000, 0.5000, 0.0000)/ (-1.51(3), 0.00, 0.00)	
Mn2b	(0.0000, 0.5000, 0.5000)/ (1.51(3), 0.00, 0.00)	
Mn2c	(0.5000, 0.0000, 0.0000)/(-1.51(3),0.00, 0.00)	
Mn2d	(0.5000, 0.0000, 0.5000)/ (1.51(3), 0.00, 0.00)	
q	(0.289(3), 0.000, 0.000)	
Magnetic Phase C		
Space group	*P1*	
Lattice parameter (Å)	a=5.73137(10), b=5.31223(11), c=7.41493(8), α=β=γ=90°	
Atom	(x,y,z)/(Mx,My,Mz)	
Mn2a	(0.0000, 0.5000, 0.0000)/ (0.44(3), -1.03(3), -0.03(3))	
Mn2b	(0.0000, 0.5000, 0.5000)/ (0.44(3), -1.03(3), 0.03(3))	
Mn2c	(0.5000, 0.0000, 0.0000)/(-0.44(3), -1.03(3), -0.03(3))	
Mn2d	(0.5000, 0.0000, 0.5000)/ (-0.44(3), -1.03(3), 0.03(3))	
Mn/Tb1a	(0.0784(3), 0.9849(1), 0.2564(1))/ (0.11(3), 0.89(3), 0.03(3))	
Mn/Tb1b	(0.9216(2), 0.0151(3), -0.2436(1))/ (0.11(3), 0.89(3), -0.03(3))	
Mn/Tb1c	(0.4216(1), 0.5151(1), -0.2436(1))/(-0.11(3), 0.89(3), 0.03(3))	
Mn/Tb1d	(0.5784(1), 0.4849(1), 0.2564(1))/ (-0.11(3), 0.89(3), -0.03(3))	
R factor[a]	R_B^1=0.058, R_F^1=0.029; R^{MB}=0.067; R^{MC}=0.038; R_B^2=0.108, R_F^2=0.106; R^M=0.089	

[a] R_B^1, R_F^1, R^{MB}, R^{MC}, R_B^2, R_F^2 and R^M are the Bragg R-factor and RF-factor of C3, Magnetic R-factor for magnetic phase B and C, the Bragg R-factor and R-factor for $Mn_{1-x-y}Tb_xCu_yO_4$, and Magnetic R-factor for $Mn_{1-x-y}Tb_xCu_yO_4$.

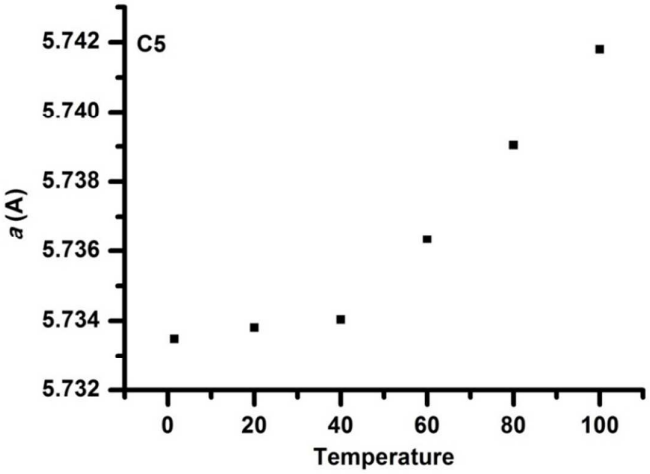

Figure S25 Temperature dependent lattice parameter *c* of C5.

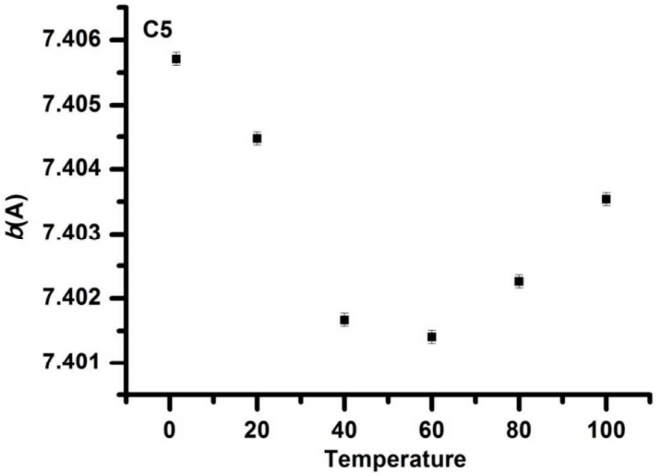

Figure S26 Temperature dependent lattice parameter *b* of C5 (in *Pnma* setting for temperature is above 40K) or *c* of C3 (in $Pna2_1$ setting for temperature is below 40K).

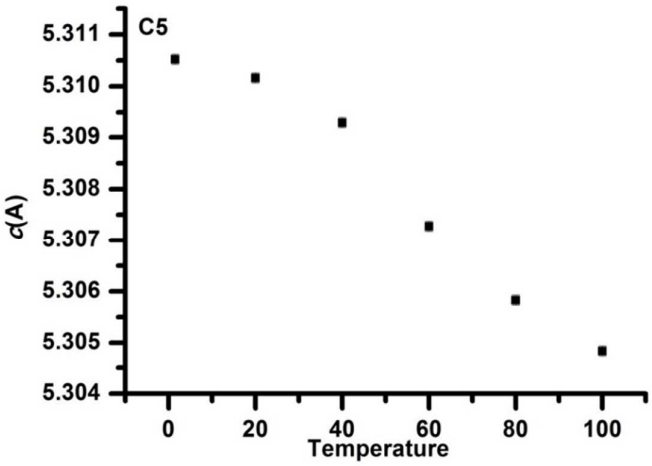

Figure S27 Temperature dependent lattice parameter *c* of C5 (in *Pnma* setting for temperature is above 40K) or *b* of C3 (in $Pna2_1$ setting for temperature is below 40K).

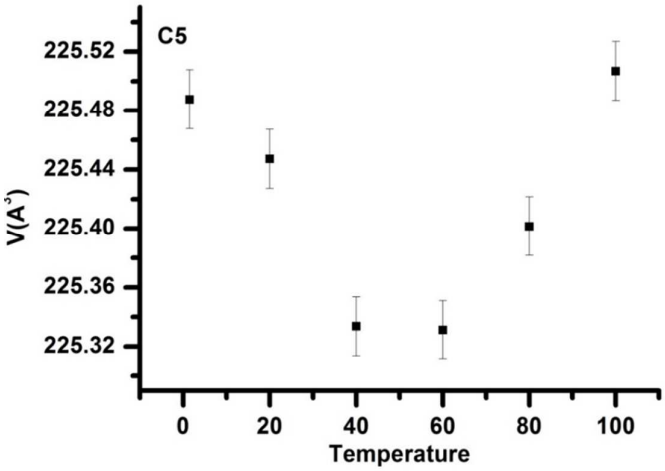

Figure S28 Temperature dependent unit cell volume V of C5.