Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Crystal Structure, Ferroelectricity and Polar Order in $Ba_4R_2Zr_4Nb_6O_{30}$ (R=La, Nd, Sm) Tetragonal Tungsten Bronze New System†

Wen Bin Feng, Xiao Li Zhu*, Xiao Qiang Liu and Xiang Ming Chen*

Electronic Supplementary Information:

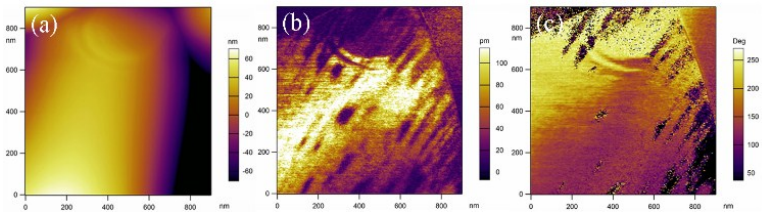

Fig. S1. PFM image of stripe like ferroelectric domains in a single grain of $Ba_4Nd_2Zr_4Nb_6O_{30}$. (a), (b) and (c) are the topography, amplitude and phase images, respectively.

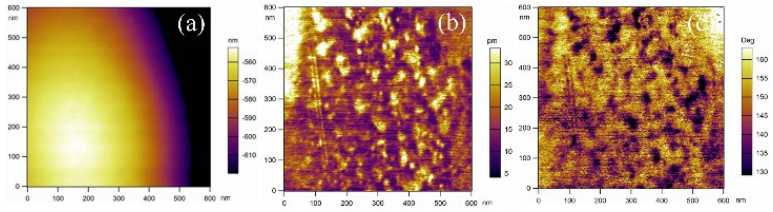

Fig. S2. PFM image of disordered local micro polar regions in a single grain of $Ba_4Sm_2Zr_4Nb_6O_{30}$. (a), (b) and (c) are the topography, amplitude and phase images, respectively.

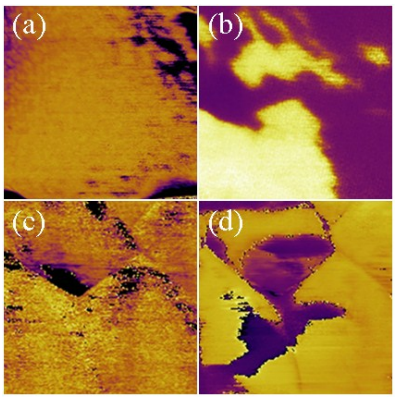

Fig. S3. PFM phase images of $Ba_4Nd_2Zr_4Nb_6O_{30}$and $Ba_4Sm_2Zr_4Nb_6O_{30}$ added with 4V AC voltage in the out-of-plane direction at the observed area for $Ba_4Nd_2Zr_4Nb_6O_{30}$(a), $Ba_4Sm_2Zr_4Nb_6O_{30}$(c), and 140V DC voltage in the same direction and area for$Ba_4Nd_2Zr_4Nb_6O_{30}$(b)and $Ba_4Sm_2Zr_4Nb_6O_{30}$(d).

Table S1. Experimental parameters for X-ray diffraction of $Ba_4R_2Zr_4Nb_6O_{30}$ (R=La,Nd,Sm)

	R=La	R=Nd	R=Sm
Unit cell	a=b=12.68891(25)Å	a=b=12.64298(26)Å	a=b=12.63063(25)Å
	c=3.99052(8)Å	c=3.97619(9)Å	c=3.97323(8)Å
Crystal system	Tetragonal	Tetragonal	Tetragonal
Z	2	2	2
Space group	P4/mbm	P4bm	P4bm
Cell volume	642.51(4)Å^3	635.57(4)Å^3	633.86(4)Å^3
$\sqrt{10}$ c/a	0.9945(0)	0.9945(3)	0.9947(6)
Reliability factors	R_{wp}=6.29	R_{wp}=7.89	R_{wp}=8.38
	R_p=4.82	R_p=6.24	R_p=6.15
	χ^2=4.882	χ^2=6.189	χ^2=6.120

Table S2. Final atomic positions of $Ba_4R_2Zr_4Nb_6O_{30}$ (R=La, Nd, Sm).

Compositions	Atom	Wyckoff position	x/a	y/b	z/c	Occupies
R=La	La1	2a	0.0(0)	0.0(0)	0.0(0)	1.0
	Ba1	4c	0.16995(7)	0.66995(7)	0.0(0)	1.0
	Zr1/Nb1	2b	0.0(0)	0.5(0)	0.5(0)	0.40/0.60
	Zr2/Nb2	8d	0.07539(10)	0.21347(9)	0.5(0)	0.40/0.60
	O1	2b	0.0(0)	0.5(0)	0.0(0)	1.0
	O2	4c	0.2782(6)	0.7782(6)	0.5(0)	1.0
	O3	8d	0.0784(9)	0.1923(8)	0.0(0)	1.0
	O4	8d	0.3387(5)	0.0012(6)	0.5(0)	1.0
	O5	8d	0.1320(8)	0.0557(9)	0.5(0)	1.0
R=Nd	Nd1	2a	0.0(0)	0.0(0)	0.8621(24)	1.0
	Ba1	4c	0.16986(9)	0.66987(9)	0.8621(22)	1.0
	Zr1/Nb1	2b	0.0(0)	0.5(0)	0.3864(26)	0.40/0.60
	Zr2/Nb2	8d	0.07480(11)	0.21207(10)	0.35131(5)	0.40/0.60
	O1	2b	0.0(0)	0.5(0)	0.901(12)	1.0
	O2	4c	0.2818(6)	0.7818(6)	0.311(5)	1.0
	O3	8d	0.0733(12)	0.1941(10)	0.919(8)	1.0
	O4	8d	0.3377(7)	0.0020(8)	0.331(17)	1.0
	O5	8d	0.1339(10)	0.0567(12)	0.469(5)	1.0
R=Sm	Sm1	2a	0.0(0)	0.0(0)	0.8854(23)	1.0
	Ba1	4c	0.16979(9)	0.66979(9)	0.88718(8)	1.0
	Zr1/Nb1	2b	0.0(0)	0.5(0)	0.4099(30)	0.40/0.60
	Zr2/Nb2	8d	0.07432(13)	0.21174(12)	0.3768(20)	0.40/0.60
	O1	2b	0.0(0)	0.5(0)	0.898(14)	1.0
	O2	4c	0.2821(7)	0.7821(7)	0.337(6)	1.0
	O3	8d	0.0751(18)	0.1831(14)	0.983(7)	1.0
	O4	8d	0.3359(8)	0.0004(10)	0.363(19)	1.0
	O5	8d	0.1356(13)	0.0543(16)	0.507(6)	1.0

Table S3. Selected bond distances for $Ba_4R_2Zr_4Nb_6O_{30}$ (R=La, Nd, Sm)

Bond distances/Å			
Compositions	R=La	R=Nd	R=Sm
R1- O(3)	2.635(8)×4	2.633(12)×4	2.530(16)×4
R1-O(5)	2.699(6)×8	2.414(15)×4	2.380(19)×4
		3.033(17)×4	3.082(22)×4
Ba1 -O(1)	3.0497(13)	3.0410(30)	3.0331(19)
Ba1 -O(2)	2.785(7)×2	2.967(19)	2.967(20)
		2.682(18)	2.686(19)
Ba1 -O(4)	2.929(5)×4	3.00(5)×2	2.99(5)×2
		2.83(5)×2	2.85(5)×2
Zr/Nb(1) -O(1)	1.99526(4)×2	1.93(5)	1.94(6)
		2.04(5)	2.03(6)
Zr/Nb(1)-O(4)	2.046(7)×4	2.063(12)×4	2.081(13)×4
Zr/Nb(2)-O(2)	2.031(4)	2.022(4)	2.026(5)
Zr/Nb(2)-O(3)	2.0136(15)×2	1.732(30)	1.604(24)
		2.270(30)	2.437(24)
Zr/Nb(2)-O(4)	1.863(7)	1.864(10)	1.831(11)
Zr/Nb(2)-O(5)	2.127(12)	2.152(16)	2.195(23)
	1.958(12)	1.990(16)	1.957(23)

Table S4. Selected bond angles for $Ba_4R_2Zr_4Nb_6O_{30}$ (R=La, Nd, Sm)

Bond angle/°			
Compositions	R=La	R=Nd	R=Sm
O(1)-Zr/Nb(1)-O(1)	180.0	180.0	180.0
O(1)-Zr/Nb(1)-O(4)	90.0×8	83.8(20)×4	84.8(21)×4
		96.2(20)×4	95.2(21)×4
O(4)- Zr/Nb(1)-O(4)	180.0×2	168(4)×2	170(4)×2
	90.9(4)×2	90.7(7)×2	89.8(8)×2
	89.1(4)×2	88.0(7)×2	89.2(8)×2
O(2)- Zr/Nb(2)-O(3)	92.11(28)×2	89.3(7)	91.0(9)
		97.4(7)	98.0(8)
O(2)-Zr/Nb(2)-O(4)	97.58(29)	95.3(4)	94.8(4)
O(2)-Zr/Nb(2)-O(5)	94.12(32)	95.9(4)	95.7(5)
	172.0(4)	169.8(8)	168.3(9)
O(3)-Zr/Nb(2)-O(3)	164.5(6)	166.7(8)	158.4(11)
O(3)-Zr/Nb(2)-O(4)	97.1(4)×2	93.6(21)	99.6(22)
		97.2(22)	99.2(24)
O(3)-Zr/Nb(2)-O(5)	82.43(33)×2	95.7(7)	91.3(10)
	86.88(26)×2	99.1(7)	98.7(10)
		72.3(6)	68.4(8)
		73.2(6)	70.7(8)
O(4)-Zr/Nb(2)-O(5)	168.3(4)	165.5(15)	164.7(18)
	90.42(33)	89.9(7)	90.1(8)
O(5)-Zr/Nb(2)-O(5)	77.9(5)	77.6(6)	77.6(8)