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Supplementary Information for

Tunable phase transitions in $NaNbO_3$ ceramics through bismuth/vacancy modification

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Table S1

EDS analysis results and elemental ratios for compositions in the system $Na_{1-3x}Bi_xNbO_3$

	$x = 0.015$	$x = 0.05$	$x = 0.10$	$x = 0.15$	$x = 0.20$
Element	Atomic%	Atomic%	Atomic%	Atomic%	Atomic%
Na	12.27	3.56	15.87	16.67	6.31
Bi	0.22	0.14	2.09	4.15	2.44
Nb	13.39	4.22	23.52	30.73	13.81
Na : Bi : Nb	0.915 : 0.016: 1	0.84 : 0.04 : 1	0.67 : 0.09 : 1	0.54 : 0.14 : 1	0.46 : 0.18 : 1

Table S2

Crystal and refinement parameters for compositions in the system $Na_{1-3x}Bi_xNbO_3$. Estimated standard deviations are given in parentheses.

Chemical formula	$Na_{0.955}Bi_{0.015}NbO_3$	$Na_{0.85}Bi_{0.05}NbO_3$	$Na_{0.7}Bi_{0.1}NbO_3$	$Na_{0.55}Bi_{0.15}NbO_3$	$Na_{0.4}Bi_{0.2}NbO_3$
Crystal system	Orthorhombic	Orthorhombic	Tetragonal	Tetragonal	Cubic
Space group	*Pbcm*	*Pbcm*	*P*4/*mbm*	*P*4/*mbm*	*Pm*-3*m*
Unit cell dimensions (Å)	a = 5.5044(2) b = 5.5653(2) c = 15.5543(5)	a = 5.5060(2) b = 5.5586(2) c = 15.6083(7)	a = 5.5321(1) c = 3.91786(9)	a = 5.5413(1) c = 3.9249(1)	a = 3.92766(7)
Volume ($Å^3$)	476.48(4)	477.70(5)	119.903(7)	120.519(8)	60.590(3)
Z	8	8	2	2	1
Density (calculated)	4.628 g/cm^3	4.752 g/cm^3	4.944 g/cm^3	5.089 g/cm^3	5.259 g/cm^3
R-factors[a]	R_{wp} = 0.0926 R_p = 0.0727 R_{ex} = 0.0466 R_F^2 = 0.1262	R_{wp} =0.0759 R_p =0.0579 R_{ex} = 0.0458 R_F^2 =0.0763	R_{wp} = 0.0819 R_p = 0.0633 R_{ex} = 0.0470 R_F^2 = 0.0749	R_{wp} = 0.0823 R_p = 0.0652 R_{ex} = 0.0475 R_F^2 = 0.0810	R_{wp} = 0.0887 R_p = 0.0715 R_{ex} = 0.0486 R_F^2 = 0.0640
No. of variables	38	38	23	23	21
No. of profile points used	3440	3440	3440	3440	3440

[a]For the definition of R-factors see ref.[1]

Table S3

Refined structural parameters for studied compositions in the system $Na_{1-3x}Bi_xNbO_3$. Estimated standard deviations are given in parentheses.

	Atom	Site	*x*	*y*	*z*	Occ.	U_{iso} (Å^2)
$Na_{0.955}Bi_{0.015}NbO_3$	Na (1)	4c	0.230(7)	0.25	0.0	0.955	0.0288(23)
	Bi (1)	4c	0.230(7)	0.25	0.0	0.015	0.0288(23)
	Na (2)	4d	0.233(6)	0.2195(32)	0.25	0.955	0.0288(23)
	Bi (2)	4d	0.233(6)	0.2195(32)	0.25	0.015	0.0288(23)
	Nb	8e	0.2526(12)	0.7362(5)	0.1244(5)	1	0.0176(4)
	O (1)	4c	0.671(8)	0.25	0.0	1	0.0113(20)
	O (2)	4d	0.223(8)	0.758(5)	0.25	1	0.0113(20)
	O (3)	8e	0.4714(34)	0.4396(30)	0.1395(16)	1	0.0113(20)
	O (4)	8e	0.016(4)	0.011(5)	0.1050(14)	1	0.0113(20)
$Na_{0.85}Bi_{0.05}NbO_3$	Na (1)	4c	0.244(6)	0.25	0.0	0.85	0.0299(14)
	Bi (1)	4c	0.244(6)	0.25	0.0	0.15	0.0299(14)
	Na (2)	4d	0.245(5)	0.2104(29)	0.25	0.85	0.0299(14)
	Bi (2)	4d	0.245(5)	0.2104(29)	0.25	0.15	0.0299(14)
	Nb	8e	0.2502(15)	0.7423(8)	0.1258(4)	1	0.01643(34)
	O (1)	4c	0.659(7)	0.25	0.0	1	0.0102(20)
	O (2)	4d	0.217(9)	0.767(6)	0.25	1	0.0102(20)
	O (3)	8e	0.488(4)	0.457(4)	0.1457(13)	1	0.0102(20)
	O (4)	8e	0.042(4)	0.032(5)	0.1185(15)	1	0.0102(20)
$Na_{0.7}Bi_{0.1}NbO_3$	Na	2c	0.0	0.5	0.5	0.7	0.0417(9)
	Bi	2c	0.0	0.5	0.5	0.1	0.0417(9)
	Nb	2a	0.0	0.0	0.0	1	0.01262(31)
	O (1)	2b	0.0	0.0	0.5	1	0.0217(18)
	O (2)	4g	0.2880(13)	0.7880(13)	0.0	1	0.0217(18)
$Na_{0.55}Bi_{0.15}NbO_3$	Na	2c	0.0	0.5	0.5	0.55	0.0480(9)
	Bi	2c	0.0	0.5	0.5	0.15	0.0480(9)
	Nb	2a	0.0	0.0	0.0	1	0.01299(36)
	O (1)	2b	0.0	0.0	0.5	1	0.0132(19)
	O (2)	4g	0.2856(14)	0.7856(14)	0.0	1	0.0132(19)
$Na_{0.4}Bi_{0.2}NbO_3$	Na	1b	0.0	0.0	0.0	0.4	0.1105(11)
	Bi	1b	0.0	0.0	0.0	0.2	0.1105(11)
	Nb	1a	0.5	0.5	0.5	1	0.0599(5)
	O	3d	0.5	0.5	0.0	1	0.0967(22)

Table S4

Selected bond lengths (Å) and bond angles (°) for studied compositions in the system $Na_{1-3x}Bi_xNbO_3$. Estimated standard deviations are given in parentheses.

	$x = 0.015$	$x = 0.05$	$x = 0.10$	$x = 0.15$	$x = 0.20$
Nb-O(1)	1.981(14)	2.027(14)	1.95893(5) ×2	1.96246(6) ×2	1.96383(3) ×6
Nb-O(2)	1.964(10)	1.951(9)	1.9783(15) ×4	1.9789(16) ×4	
Nb-O(3)	2.056(18)	2.080(24)			
Nb-O(3)′	1.909(19)	1.896(21)			
Nb-O(4)	1.963(26)	1.983(26)			
Nb-O(4)′	2.030(28)	1.989(23)			
Na (1)-O(1)	3.08(5)	2.29(5)	2.76606(5) ×4	2.77065(7) ×4	2.77728(5) ×4
Na (1)-O(1)′	2.43(5)	2.830(11) ×2			2.77728(3) ×8
Na (1)-O(1)″	2.836(12) ×2				
Na (1)-O(2)			2.986(7) ×4	2.977(8) ×4	
			2.567(6) ×4	2.583(7) ×4	
Na (1)-O(3)	2.754(28) ×2	2.883(25)			
Na (1)-O(3)′	3.224(29) ×2	3.160(28) ×2			
		2.883(25)			
Na (1)-O(4)	2.412(29) ×2	2.475(26) ×2			
Na (1)-O(4)′	2.572(34) ×2	2.891(30) ×2			
Na (2)-O(2)	2.571(30)	2.47(4)			
Na (2)-O(2)′	2.995(30)	3.10(4)			
Na (2)-O(2)″	2.52(5)	2.57(5)			
Na (2)-O(2)‴	3.00(5)	2.98(5)			
Na (2)-O(3)	2.487(31) ×2	2.516(31) ×2			
Na (2)-O(3)′	2.835(28) ×2	2.603(27) ×2			
Na (2)-O(4)	2.801(26) ×2	2.539(26) ×2			
Na (2)-O(4)′	3.098(29) ×2	3.148(28) ×2			
O(1)-Nb-O(3)	91.0(13)	90.3(11)			
O(1)-Nb-O(3)′	85.8(15)	87.6(13)			
O(1)-Nb-O(4)	92.1(12)	98.9(10)			
O(1)-Nb-O(4)′	87.8(15)	94.0(8)			
O(2)-Nb-O(3)	89.0(13)	88.0(14)			
O(2)-Nb-O(3)′	84.7(14)	82.2(15)			
O(2)-Nb-O(4)	97.4(15)	91.3(19)			
O(2)-Nb-O(4)′	92.8(14)	86.9(17)			
O(3)-Nb-O(3)′	89.8(4)	88.7(4)			
O(3)-Nb-O(4)	87.0(11)	94.1(13)			
O(3)′-Nb-O(4)′	94.7(11)	86.3(13)			
O(4)-Nb-O(4)′	88.6(4)	90.3(4)			
O(1)-Nb-O(1)			180	180	90
O(1)-Nb-O(2)			90	90	
Nb-O(1)-Nb	155.4(25)	151.5(25)	180	180	180
Nb-O(2)-Nb	168.3(23)	166.6(28)	162.7(6)	163.8(6)	
Nb-O(3)-Nb	158.1(15) ×2	159.1(14)			
Nb-O(4)-Nb	160.3(16) ×2	160.3(14)			

Table S5

Comparison of the Raman band positions (cm^{-1}) for $Na_{0.955}Bi_{0.015}NbO_3$ in this work with those reported for $NaNbO_3$

$NaNbO_3$ (*Pbcm*) Band positions [2]	$Na_{0.955}Bi_{0.015}NbO_3$ (*Pbcm*) Band positions	Assignment	Ref.
121.0	120.39		
142.1	140.30		
153.4	154.37		
175.1	176.72	ν_6	2, 3
183.2	186.19		
201.0	203.22		
218.8	219.35		
247.6	252.87	ν_5	2, 3
276.1	274.71		
295.9	293.11	ν_4	2, 3
378.5	328.46		
435.3	434.04	ν_2	2, 3
557.2	556.34	ν_1	2, 3
602.6	599.68		
671.5	637.18	ν_3	2, 3
867.3	856.90	$\nu_5 + \nu_1$	2, 3

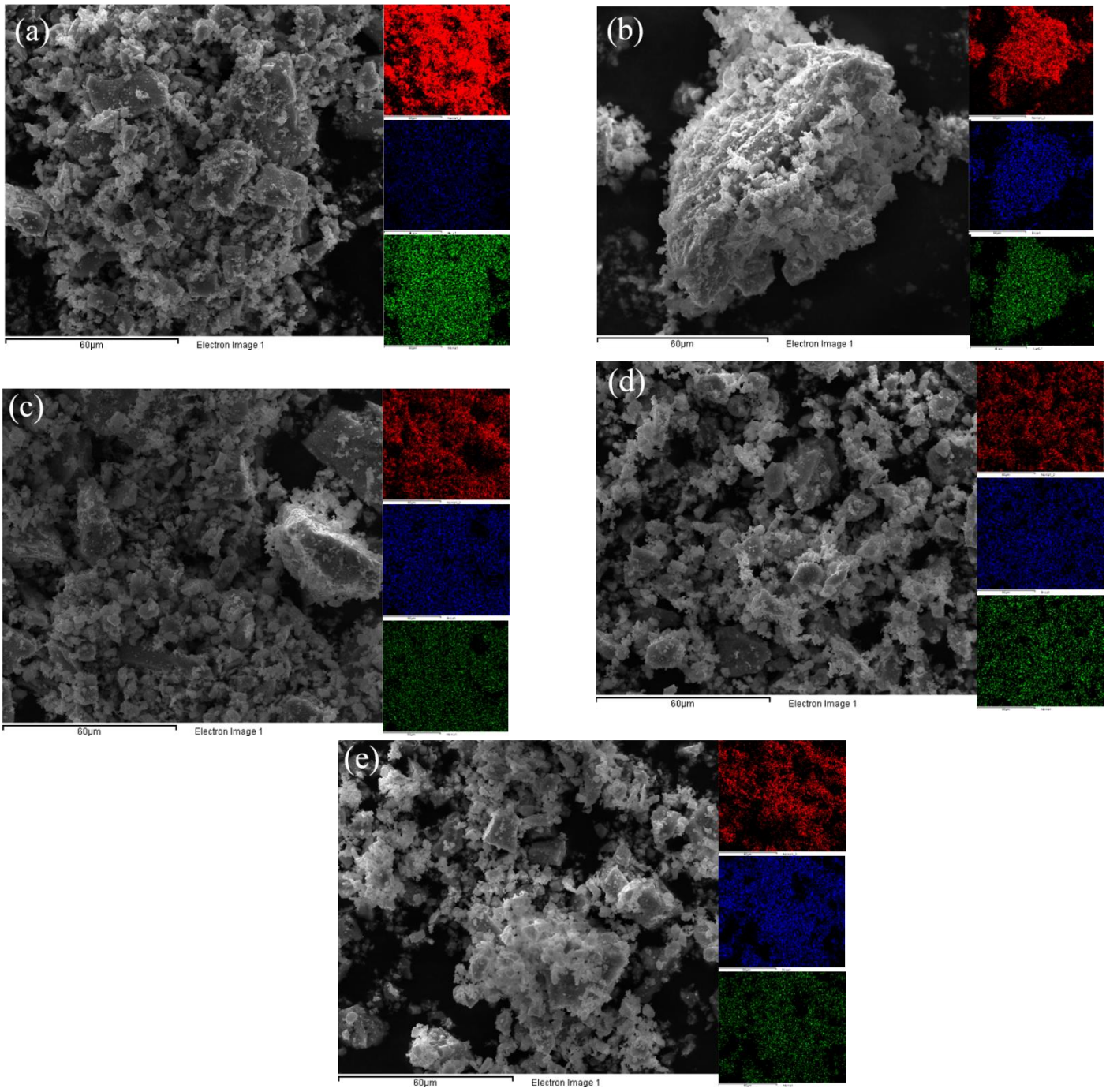

Fig. S1

SEM images used for EDS analysis and corresponding element mapping (Na (red), Bi (blue), Nb (green)) for (a) x = 0.015, (b) x = 0.05, (c) x = 0.10, (d) x = 0.15 and (e) x = 0.20 compositions in the system $Na_{1-3x}Bi_xNbO_3$

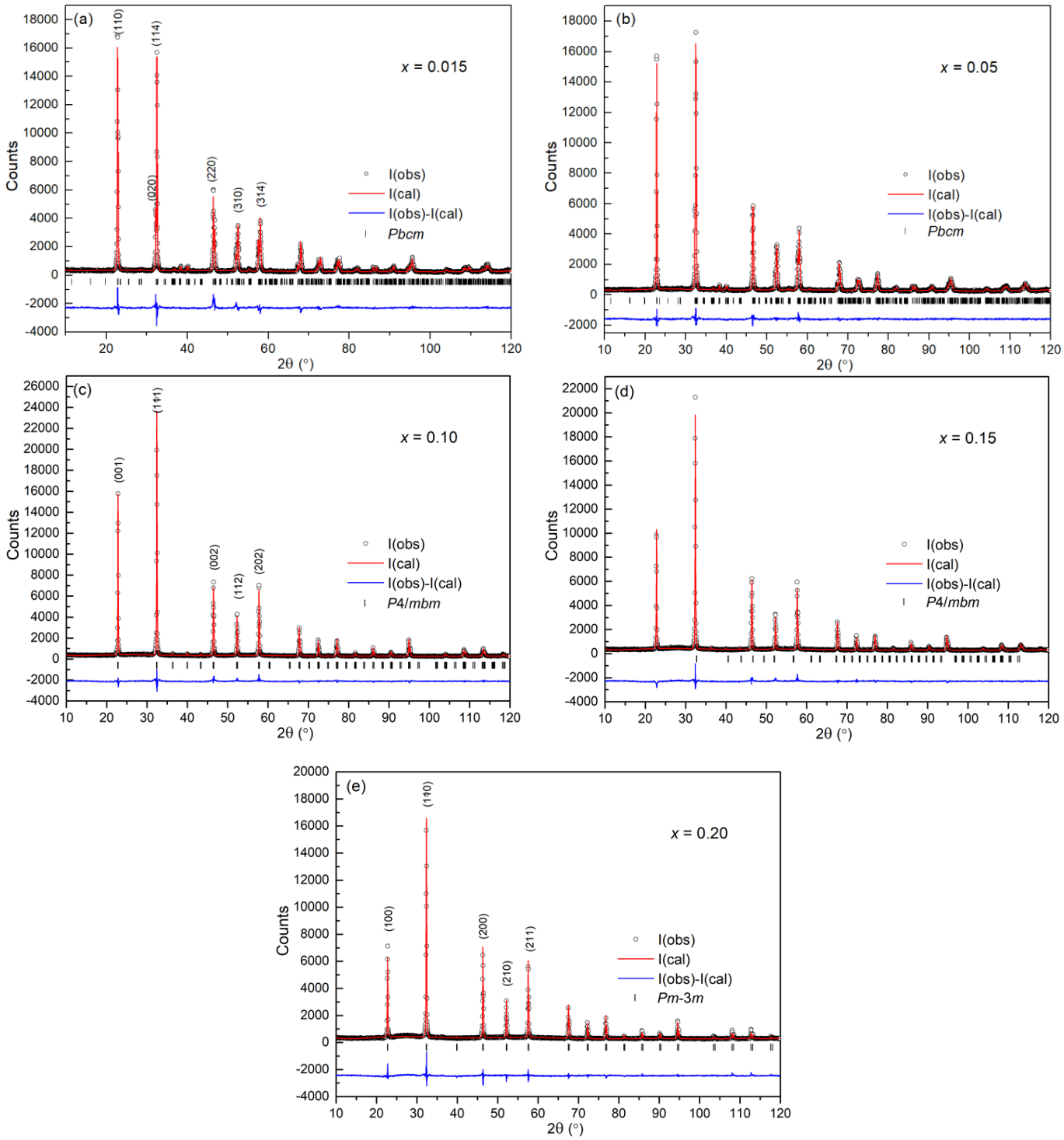

Fig. S2

Fitted diffraction profiles for (a) x = 0.015, (b) x = 0.05, (c) x = 0.10, (d) x = 0.15 and (e) x = 0.20 compositions in the system $Na_{1-3x}Bi_xNbO_3$, showing observed (○ symbols), calculated (red line) and difference (blue line) profiles. Reflection positions are indicated by markers.

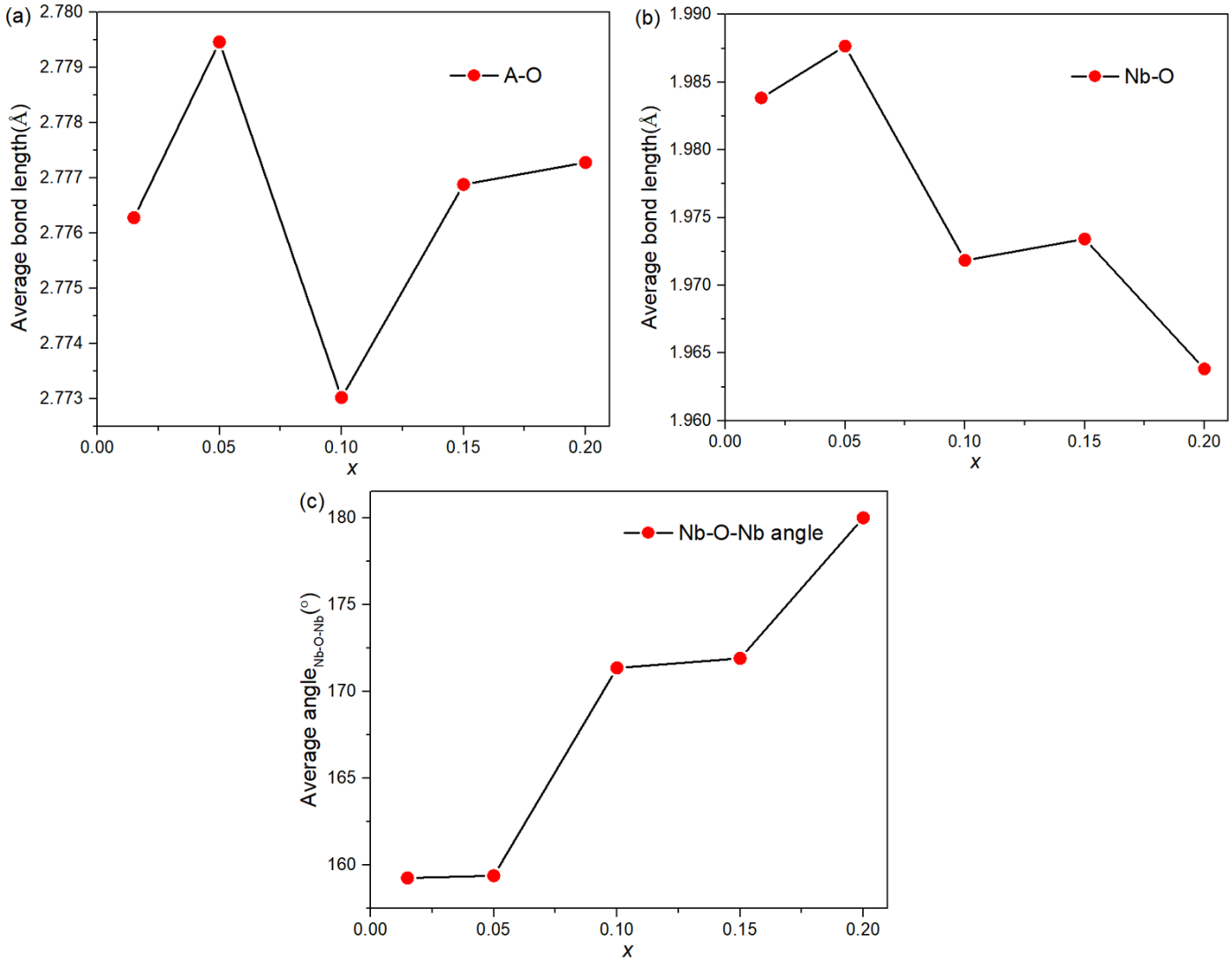

Fig. S3

Compositional variation of (a) average A-O (A = Na, Bi, Vac) bond length, (b) average Nb-O bond length and (c) average Nb-O-Nb bond angle in the $Na_{1-3x}Bi_xNbO_3$ system.

References

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3. X. B. Wang, Z. X. Shen, Z. P. Hu, L. Qin, S. H. Tang and M. H. Kuok, *J. Mol. Struct.*, 1996, **385**, 1-6.