Supporting Information

Enhanced Visible Photocatalytic Hydrogen Evolution of KN-based Semiconducting Ferroelectrics *via* Bandgap Engineering and High-field Poling

Yuchen Lan [1], Zhihai Sun [1], Changlai Yuan[,1, 2], Xiaogang Xue [1], Jun Chen**[,2], Lei Miao [1, 3], Yiping Guo [4], Changrong Zhou [1], Jiwen Xu [1], Jianhua Zhou***[,1], Jiang Wang [1], Guanghui Rao****[, 1, 5]*

[1] Guangxi Key Laboratory of Information Materials, School of Material Science and Engineering, Guilin University of Electronic Technology, Guilin 541004, PR China

[2] School of Mathematics and Physics, University of Science and Technology Beijing, Beijing 100083, PR China

[3] Department of Materials Science and Engineering, SIT Research Laboratories, Innovative Global Program, Faculty of Engineering, Shibaura Institute of Technology, Tokyo 1358548, Japan

[4] State Key Laboratory of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

[5] Institute of Physics, Chinese Academy of Sciences, Beijing 100190, PR China

[†]Corresponding authors. Changlai Yuan, Email: yuanchanglai@guet.edu.cn*

*Jun Chen**, Email: junchen@ustb.edu.cn*

*Jianhua Zhou***, Email: jianhuazhou@guet.edu.cn*

*Guanghui Rao****, Email: rgh@guet.edu.cn*

Table S1. Refined crystal parameters of the (1-*x*)KN-*x*BNB samples' unit cell through Fullprof suite software.

Parameters	x = 0.00	x = 0.01		x = 0.02		x = 0.03		x = 0.04		x = 0.05	
Sig	3.15	1.37		1.26		1.08		1.06		1.05	
R_{wp} (%)	13.3	9.40		9.53		8.24		8.89		8.63	
R_{exp} (%)	7.51	8.03		8.47		7.90		8.62		8.14	
Space group	*Amm2*	*Amm2*	*P4mm*	*Amm2*	*P4mm*	*Amm2*	*P4mm*	*Amm2*	*P4mm*	*Amm2*	*P4mm*
Symmetry	*O* phase	*O* phase	*T* phase	*O* phase	*T* phase	*O* phase	*T* phase	*O* phase	*T* phase	*O* phase	*T* phase
Fraction (%)	100	94.70	5.30	74.64	25.36	64.63	35.37	60.18	39.82	73.68	26.32
a (Å)	3.9980	4.0060	3.9856	4.0106	3.9989	4.0102	4.0026	4.0126	4.0050	4.0131	4.0025
b (Å)	5.6979	5.6899	3.9856	5.6873	3.9989	5.6838	4.0026	5.6832	4.0050	5.6862	4.0025
c (Å)	5.6973	5.6876	4.0393	5.6910	4.0400	5.6864	4.0353	5.6897	4.0388	5.6863	4.0403
c/*a*	1.4250	1.4197	1.0134	1.4189	1.0103	1.4179	1.0081	1.4179	1.0084	1.4169	1.0094
$\alpha=\beta=\gamma$ (º)	90 º	90 º	90 º	90 º	90 º	90 º	90 º	90 º	90 º	90 º	90 º
V (Å^3)	129.784	129.642	64.163	129.811	64.605	129.611	64.649	129.749	64.784	129.759	64.726
Z	2	2	1	2	1	2	1	2	1	2	1

Table S2. Refined crystal parameters of 0.99KN-0.01BNB sample unit cell under different high-field polarization conditions.

Parameters	Unpoled		Poled condition 1		Poled condition 2		Poled condition 3		Poled condition 4	
Sig	1.37		1.76		1.57		1.89		1.99	
R_{wp} (%)	9.4		10.6		11.2		11.6		11.2	
R_{exp} (%)	8.03		8.03		8.69		8.39		7.92	
Space group	*Amm2*	*P4mm*	*Amm2*	*P4mm*	*Amm2*	*P4mm*	*P4mm*	*P4mm*	*Amm2*	*P4mm*
Symmetry	*O* phase	*T* phase	*O* phase	*T* phase	*O* phase	*T* phase	*O* phase	*T* phase	*O* phase	*T* phase
Fraction (%)	94.70	5.30	61.47	38.53	69.19	30.81	73.03	26.97	73.88	26.12
a (Å)	4.0060	3.9856	3.9913	4.0088	4.0052	4.0189	4.0208	4.0409	4.0222	4.0398
b (Å)	5.6899	3.9856	5.6947	4.0088	5.7101	4.0189	5.6783	4.0409	5.6826	4.0398
c (Å)	5.6876	4.0393	5.6878	4.0147	5.7007	4.0179	5.6826	4.0419	5.6838	4.0485
c/*a*	1.4197	1.0134	1.4250	1.0014	1.4233	0.9997	1.4133	1.0002	1.4131	1.0021
$\alpha=\beta=\gamma$ (º)	90 º	90 º	90 º	90 º	90 º	90 º	90 º	90 º	90 º	90 º
V (Å^3)	129.642	64.163	129.279	64.517	130.375	64.897	129.742	64.000	129.910	66.073
Z	2	1	2	1	2	1	2	1	2	1

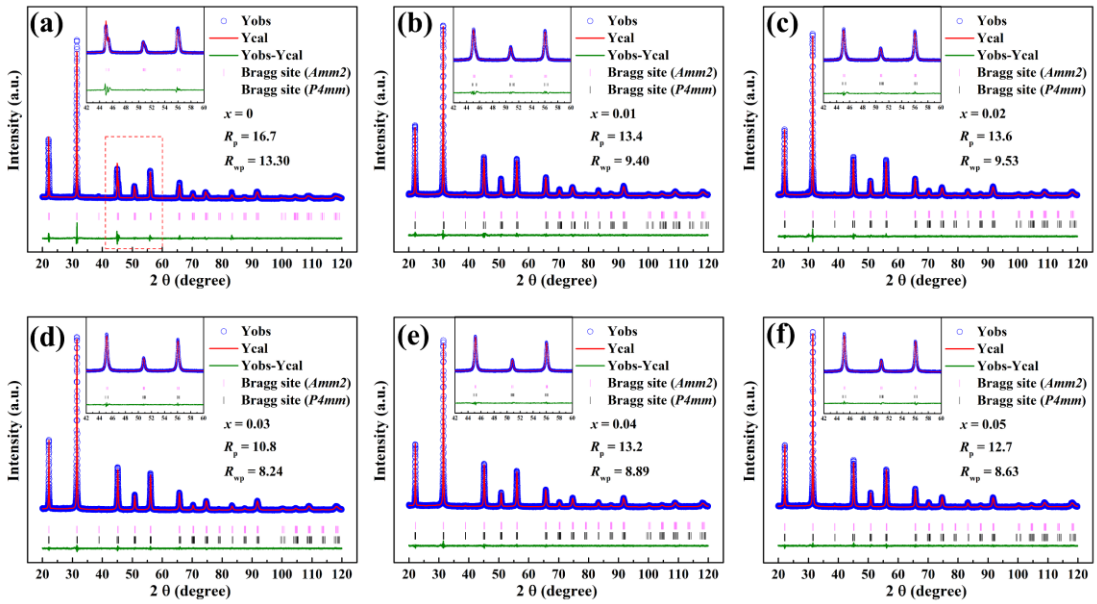

Figure S1 Refined XRD profiles of (1-*x*)KN-*x*BNB samples **(a)** x = 0, **(b)** x = 0.01, **(c)** x = 0.02, **(d)** x = 0.03, **(e)** x = 0.04, **(f)** x = 0.05. The insets show the enlarged fitting results of 2θ = 42-60°.

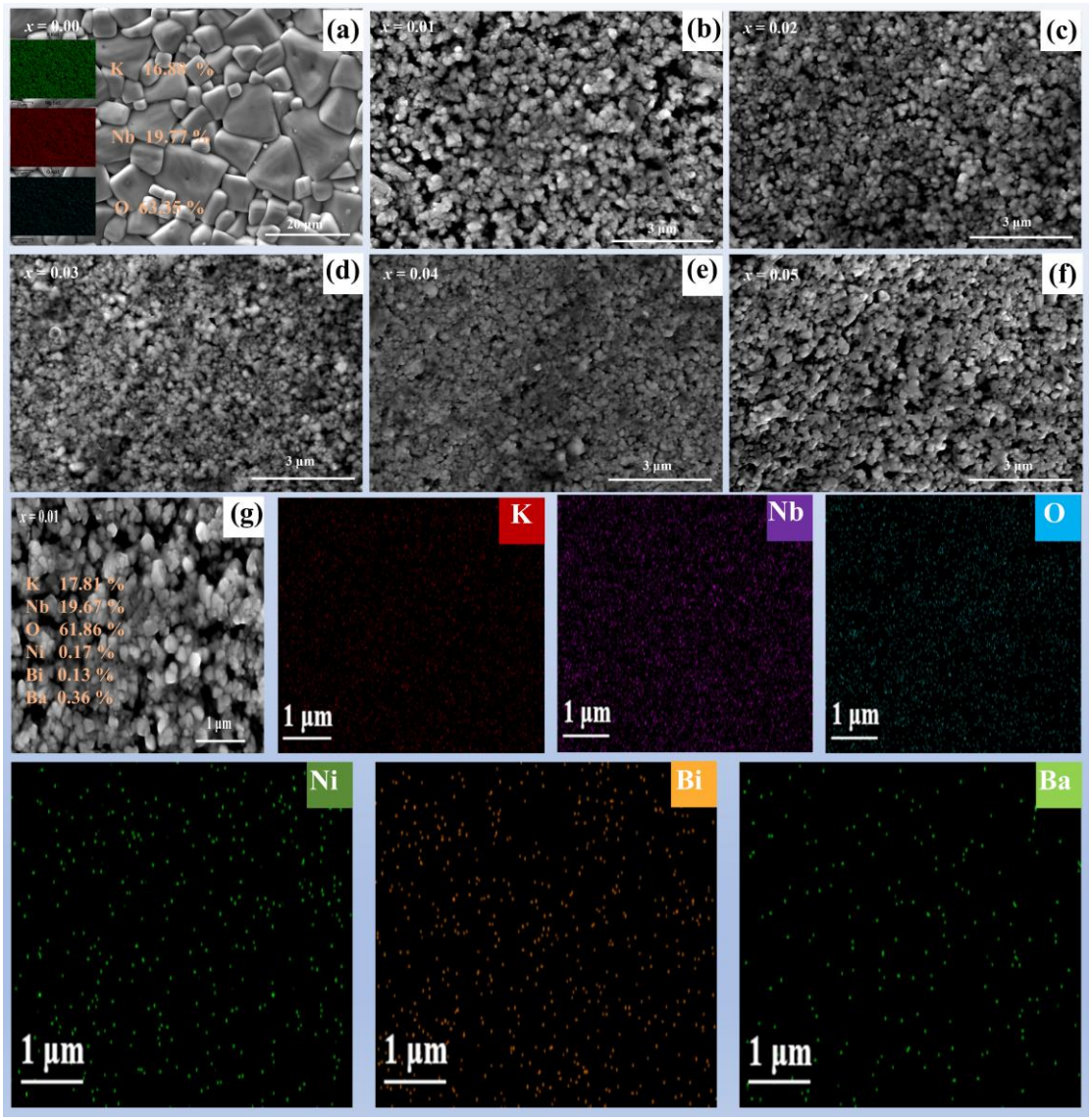

Figure S2 SEM images of (1-*x*)KN-*x*BNB samples **(a)** *x* = 0, **(b)** *x* = 0.01, **(c)** *x* = 0.02, **(d)** *x* = 0.03, **(e)** *x* = 0.04, **(f)** *x* = 0.05 and **(g)** elemental mapping of *x* = 0.01.

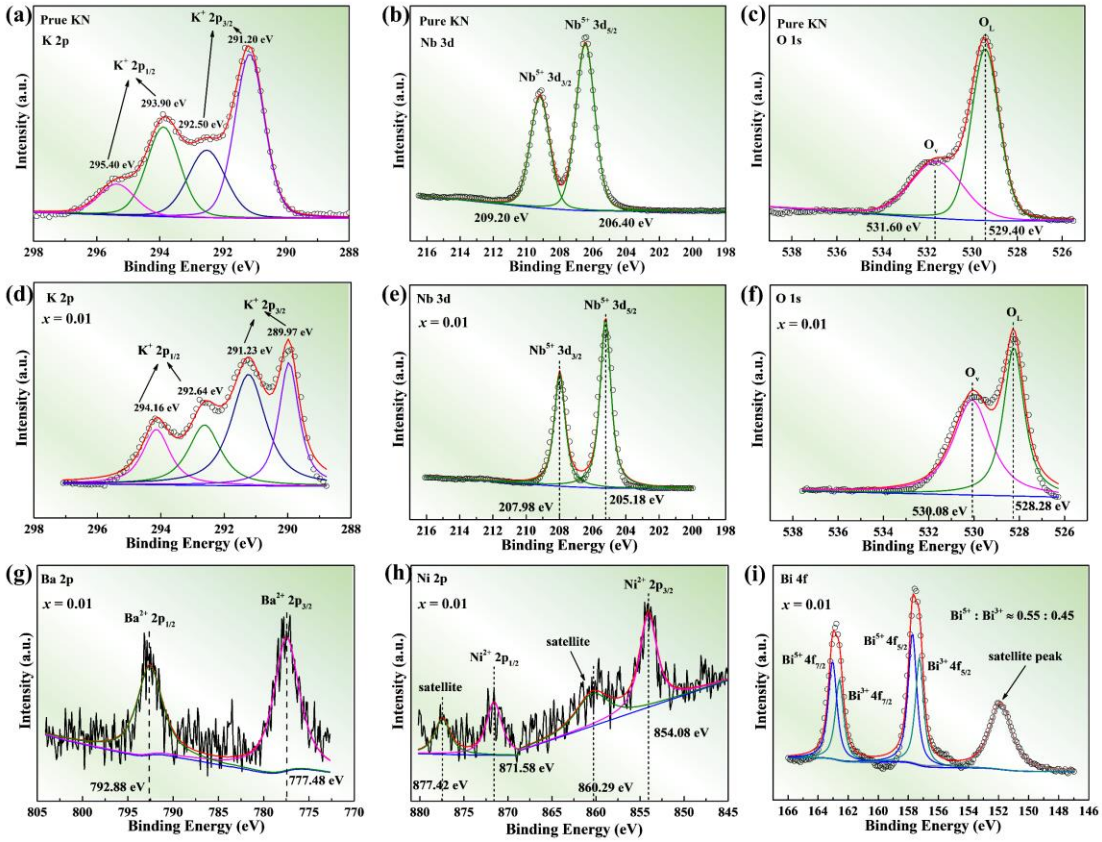

Figure S3 XPS spectrum of the pure KN **(a)** K 2p; **(b)** Nb 3d; **(c)** O 1s and the 0.99KN-0.01BNB **(d)** K 2p; **(e)** Nb 3d; **(f)** O 1s; **(g)** Ba 2p; **(h)** Ni 2p; **(i)** Bi 4f.

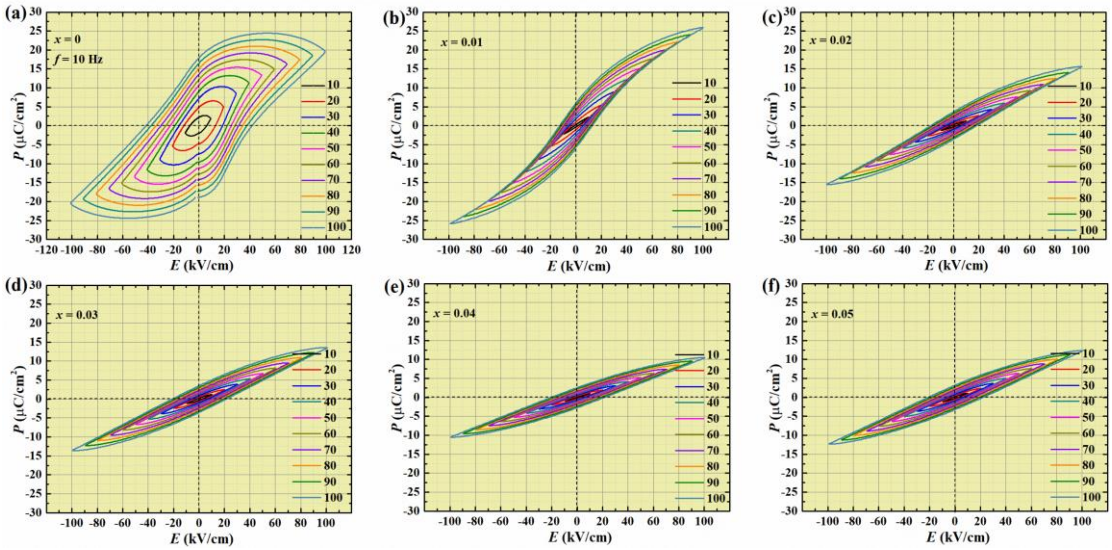

Figure S4. *P*-*E* loops of (1-*x*)KN-*x*BNB samples **(a)** *x* = 0, **(b)** *x* = 0.01, **(c)** *x* = 0.02, **(d)** *x* = 0.03, **(e)** *x* = 0.04, **(f)** and *x* = 0.05 at room temperature (*E* = 10-100 kV/cm, *f* = 10 Hz).

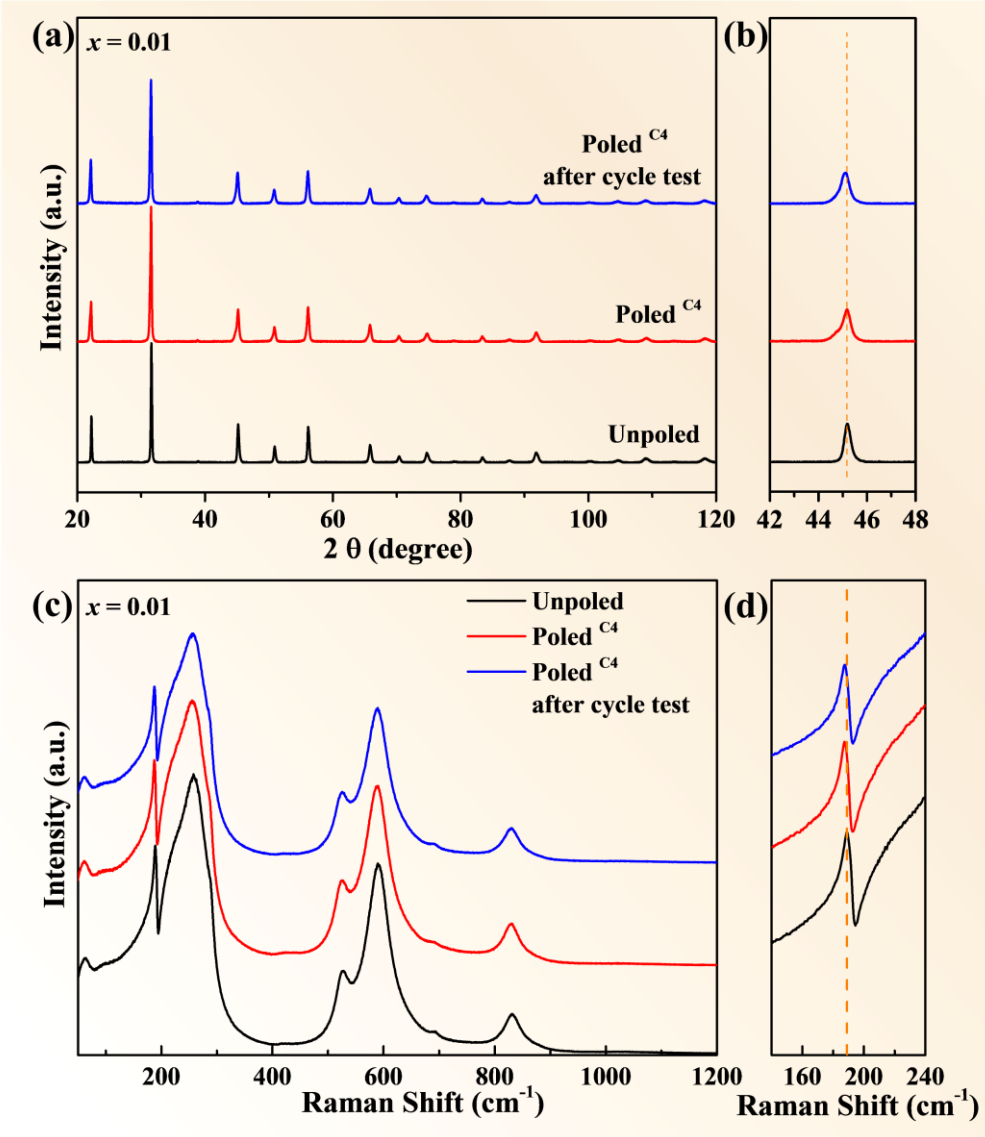

Figure S5. (a) XRD patterns of the unpoled, poled ^{C4} and the poled ^{C4} after PHE cycle test (x = 0.01); **(b)** enlarged plots of 2θ = 42-48°; **(c)** Raman spectra of the unpoled, poled ^{C4} and the poled ^{C4} after PHE cycle test (x = 0.01); **(d)** enlarged plots of B_1(TO) vibration model.

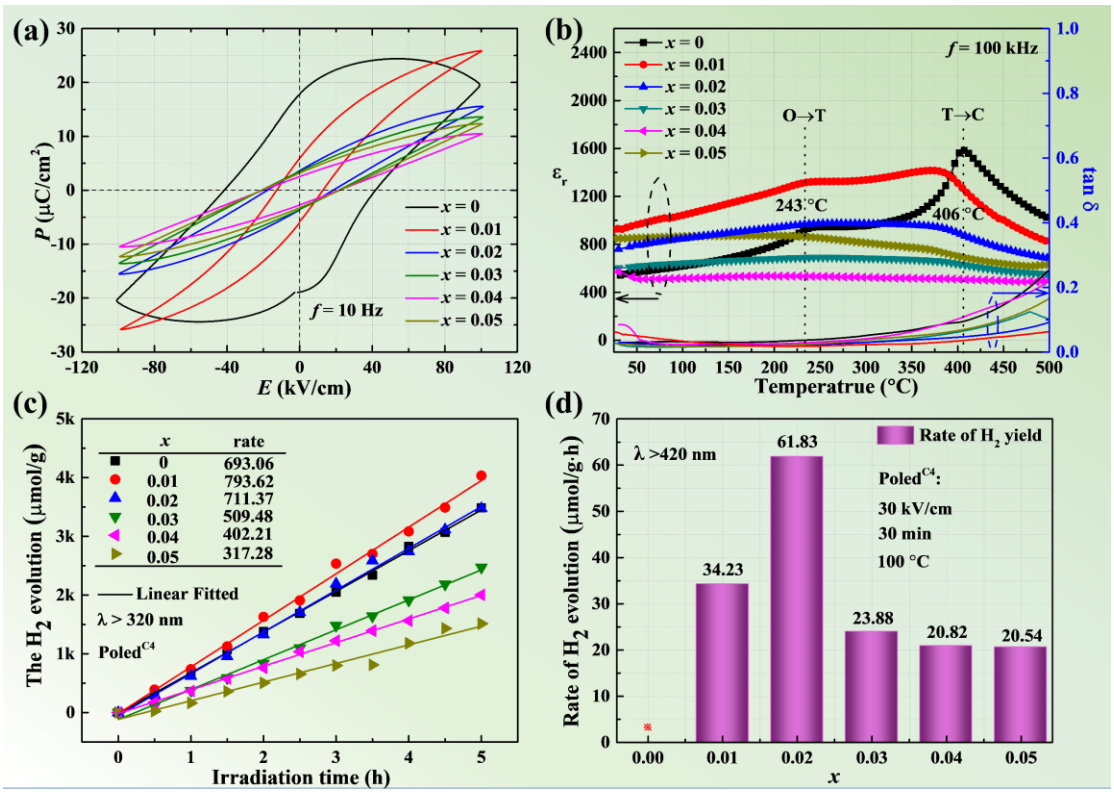

Figure S6. (a) *P-E* loops of (1-*x*)KN-*x*BNB ceramics at 100 kV/cm; **(b)** Raman spectrum of (1-*x*)KN-*x*BNB; **(c)** full-spectrum PHE rate of (1-*x*)KN-*x*BNB at poled ^{C4} and **(d)** the corresponding visible-light PHE rate.

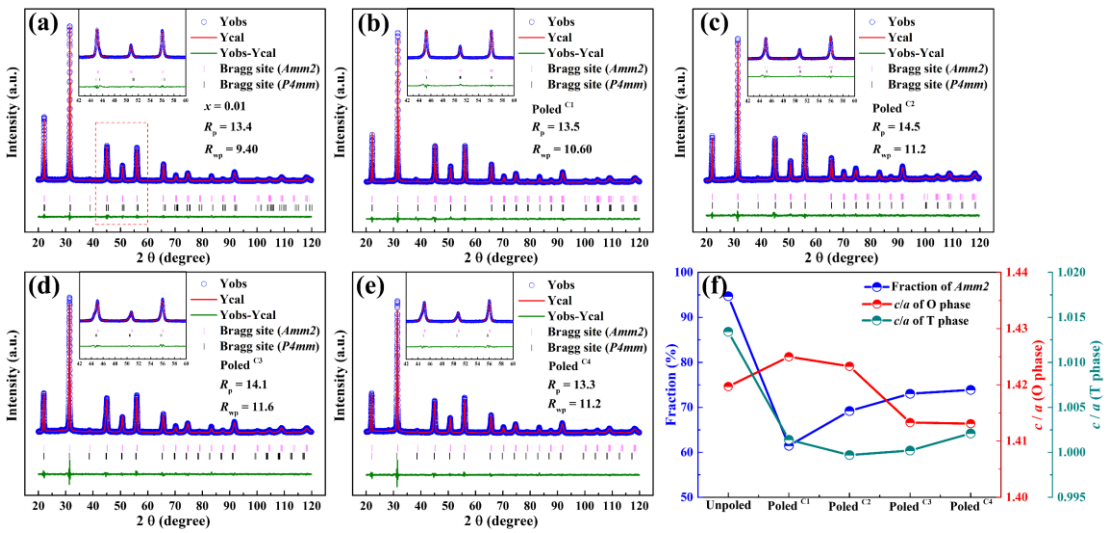

Figure S7. (a) Refined XRD profiles of 0.99KN-0.01BNB samples poled at different conditions **(a)** unpoled **(b)** poled ^{C1} **(c)** poled ^{C2} **(d)** poled ^{C3} **(e)** poled ^{C4} and the insets show the enlarged view of 2θ = 42-60°. **(f)** The change of phase fraction and *c/a* value in O phase and T phase with different polarization conditions.

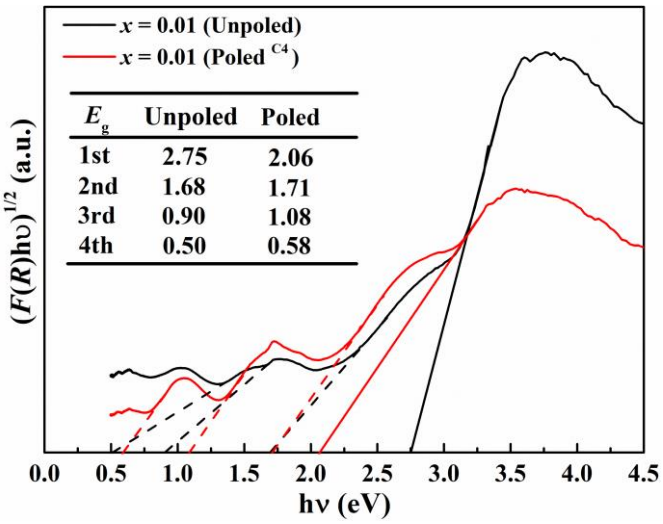

Figure. S8 Indirect bandgaps of unpoled and poled ^{C4} samples extrapolated by Tauc plots.