Supplementary Information

The Novel Behaviours of Multiferroic Properties in Na Doped BiFeO₃ Nanoparticles

Hong Zhang, ^a Weifang Liu, ^{*a} Ping Wu, ^a Xiao Hai, ^{ae} Minchen Guo, ^a Xiaojuan Xi, ^b Ju Gao, ^c Xu Wang, ^b Feng Guo, ^b Xunling Xu, ^a Can Wang, ^d Guangyao, Liu ^d Weiguo Chu ^e and Shouyu Wang, ^{*bc}

^{*a*} Tianjin Key Laboratory of Low Dimensional Materials Physics and Preparing Technology, Faculty of Science, Tianjin University, Tianjin 300072, P. R. China.

^b College of Physics and Material Science, Tianjin Normal University,

Tianjin 300074, P. R. China.

^c Department of Physics, the University of Hong Kong, Pokfulam Road, Hong Kong.

^d Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, P. R. China.

^e National Center For Nanoscience and Technology of China, Beijing 100190, P. R. China.

* Corresponding author W F Liu: Department of Applied Physics, Faculty of Science, Tianjin University, Tianjin 300072, China Tel.: +86-22-27403488; Fax: +86-22-27406852 E-mail: <u>wfliu@tju.edu.en</u>

^{*} Corresponding author S Y Wang: College of Physics and Materials Science, Tianjin Normal University, Tianjin 300387, China Tel.: +86-22-23766503; E-mail: shouyu.wang@yahoo.com

1. The Rietveld refinement of X-ray diffraction

The crystalline structure analysis of all the samples was carried out by X-ray diffraction (XRD) using Rigaku D/MAX-2500 diffractometer. The XRD measurements were carried out at room temperature using Cu K α radiation source ($\lambda = 1.5406$ Å, operated at 45 kV and 200 mA). The data of the samples were collected in the range $2\theta = 20^{\circ}$ to 100° with the step size 0.02° and 1 second count time at each step. The samples were placed in zero background sample holder for the measurement purpose. Fullprof suite (Version 5.40, March 2014) was used for Rietveld refinement.¹ The refined structural parameters obtained from the refinement for the pure and doped samples are summarized in Table S1.

Parameters		Compositions			
		X=0	X=0.01	X=0.03	X=0.05
Space group		R3c (161)	R3c (161)	R3c (161)	R3c (161)
Lattice	a (Å)	5.577	5.577	5.577	5.577
parameters	c (Å)	13.867	13.866	13.856	13.853
	Volume(Å ³)	373.57	373.52	373.24	373.14
Average bond	Bi–O	2.377	2.325	2.328	2.384
length (Å)	Fe–O	1.863	1.912	1.910	1.889
	Fe–O	2.173	2.139	2.137	2.149
Average bond	Fe–O–Fe	155.68	156.14	156.49	157.81
angle (Å)	O–Bi–O	75.24	74.19	74.22	74.83
	R _p	7.79	7.48	8.06	9.6
R-factors (%)	R_{wp}	10.8	9,92	10.8	13.0
	R _{exp}	5.41	5.04	4.9	5.41
Bragg R-factor (%)		4.16	3.06	2.86	4.49
R _f -factor (%)		2.74	2.28	1.97	2.77

Table S1. Refined structural parameters of $Bi_{1-x}Na_xFeO_3$ (x=0, 0.01, 0.03, 0.05) nanoparticles.

2. The selected area electron diffraction (SAED) pattern and the high resolution TEM (HRTEM)

The average particle size and microstructural properties of the samples were investigated by transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and the corresponding selected area electron diffraction (SAED) pattern using JEM-2100F instrument. The selected area electron diffraction (SAED) pattern and the high resolution TEM (HRTEM) obtained from an individual nanoparticle are shown in the Figure S1.



Figure S1. The selected area electron diffraction (SAED) pattern and the high resolution TEM (HRTEM) images of (a), (b) undoped BFO nanoparticle and (c), (d) 1% Na-doped BFO nanoparticle, respectively.

3. X-ray photoelectron spectroscopy (XPS)

The X – ray photoelectron spectroscopy (XPS) spectra of the samples were recorded using PHI1600. Figure S2 shows survey scans of undoped and Na-doped BiFeO₃ samples. XPS

studies reveal the presence of Bi, Fe, O elements for undoped BiFeO₃ sample and Bi, Fe, O, Na elements for Na-doped BiFeO₃ sample without any other trace of impurities except a small trace of adsorbed carbon C1s at 285 eV that was used to calibrate the system. Thus, high purity of the samples was confirmed in XPS studies.



Figure S2 The XPS survey scans of all the samples indicating elements present in the samples.

1. C. J. Rodriguez, Rietveld and pattern matching analysis program; Laboratoire Leon Brillouin,

CEA-CNRS, France (FULLPROF (March 2014)).