Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Coupling Oxygen Vacancy Gradient Distribution and Flexoelectric Effect for Enhanced Photovoltaic Performance in Bismuth Ferrite Films

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1. Ferroelectric properties:

Figure S1 shows the ferroelectric polarization (P) of BSFNO-g thin film measured at 5KHz as a function of electric field (E). Gradient-doped BSFNO-g thin film exhibits weak ferroelectric behavior due to large leakage possibly derived from oxygen vacancies, since the polarization is only ~20μm/cm^2 under the maximum electric field of 800kV/cm (Fig. S1a). As shown in Fig. S1b, the displacement current of BSFNO-g film does not show a sharp increase as the applied electric field is beyond the coercive field, which indicates that the film does not show obvious current switching behavior. Due to the gradient distribution of oxygen vacancies caused by gradient doping, the polarization conversion process seems to be inhibited in the BSFNO-g film to a certain extent. In conclusion, the BSFNO-g sample surely exhibit the ferroelectric nature, although the polarization reversal seems to be inhibited by the gradient distribution of oxygen vacancies. It means that the dopants of Sm and Ni do not excessively disturb the intrinsic ferroelectric nature of $BiFeO_3$, which is well consistent with the analysis on the XRD results.

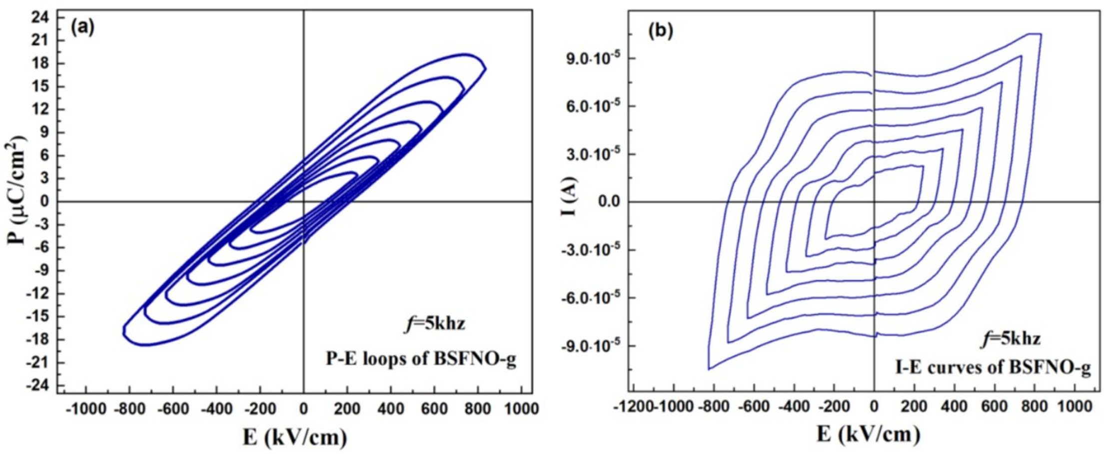

Figure S1 *(a) Relationship curves between ferroelectric polarization(P) and electric field(E) (b) Relationship curves between current(I) and electric field(E)*

2. Estimation of the strain gradient:

In order to obtain the vertical strain gradient $\partial u/\partial z$ for the estimation of the strain gradient in the film, the X-ray diffraction peak broadening at several special angles was carefully analyzed to draw the Williamson Hall (W-H) diagram. The strain gradient of the 210nm BSFNO-g film was herein estimated on the basis of the Williamson Hall (W-H) relationship, which can be described as follows [37-40]:

$$\beta cos\theta = k_0 + 4u_i sin\,\theta \#S1$$

Where $\beta = \beta_{meas} - \beta_{inst}$. β_{meas} is the width at half maximum of the measured diffraction peak. β_{inst} is the device broadening. θ is the diffraction angle. u_i is the out of plane non-uniform strain.

Obviously, it is necessary to analyze the X-ray diffraction peak broadening so as to calculate the out of plane non-uniform strain (u_i). In this case, three pseudo-cubic Bragg peaks $(001)_{PC}$, $(002)_{PC}$ and $(003)_{PC}$ in the XRD data were chosen and fitted by Gaussian functions (Fig. S2a, b and c). Obtained from Fig. S2a, b and c, the data of β and θ are plotted in Fig. S2d, so-called as Williamson Hall (W-H) diagram [38]. Therefore, u_i can be extracted from the Williamson Hall (W-H) plots according to Formula S1.

According to the strain distribution model independent of the actual relaxation mechanism, the in-plane strain $u(z)$ can be described as follows [37-40]:

$$u(z) = u_0 e^{\frac{-z}{\delta}} = u_0\left[cosh\frac{z}{\delta} - tanh\frac{t}{\delta} * sin\,h\frac{z}{\delta}\right]\#S2$$

Where u_0 is strain at the film substrate interface, δ is Penetration depth of strain. u_0 and δ are all constants. Z is the distance from the film substrate interface; T is the thickness of the film (210nm for BSFNO-g film).

If the above general model (Formula S2) exhibits exponential strain relaxation, the following relationship can be achieved:

$$tanh\frac{t}{2\delta} = \frac{t}{2\delta} * \frac{\bar{u}^2}{\bar{u}^2 + u_i^2} \#S3$$

Where $\bar{u}$ is average strain, which can be calculated by the following Formula S4:

$$\bar{u} = \frac{a_{film}}{a_{bulk}} - 1 \#S4$$

Including: a_{film} is average out-of-plane lattice constant of the film, a_{bulk} is bulk lattice constant (3.952Å).

Combining Formula S1, formula S2 and formula S3, the two constants of u_0 and δ can be calculated. Then, the average vertical strain gradient in the 210nm thick BSFNO-g film was estimated using the following Formula S5:

$$\left(\frac{\bar{\partial u}}{\partial z}\right) = \frac{\int_0^t \frac{\partial u}{\partial z} dz}{t} = \frac{u_0 * e^{-\frac{0.27 * 10^{-6}}{\delta}} - u_0}{0.27 * 10^{-6}} \#S5$$

By adding the values of u_0 and δ into Formula S5, the average vertical strain gradient $\partial u/\partial z$ in the BSFNO-g film with a thickness of f 210nm could be estimated to be 0.21×10^5/m.

As shown in Figure S2, according to the Williamson hall relationship, the vertical strain gradient in the 210nm thick BSFNO-g film was estimated to be 0.21×10^5/m. Therefore, the flexoelectric field E_{flexo} in the 210nm thick BSFNO-g film is about 0.36×10^5 V/m. Although E_{flexo} in BSFNO-g thin film is not as large as ~ 10^6V/m found in the epitaxial $BiFeO_3$ thin films with large mismatch strain, it is sufficient to affect the separation of photogenerated carriers, thereby improving the photovoltaic performance of BSFNO-g thin film.

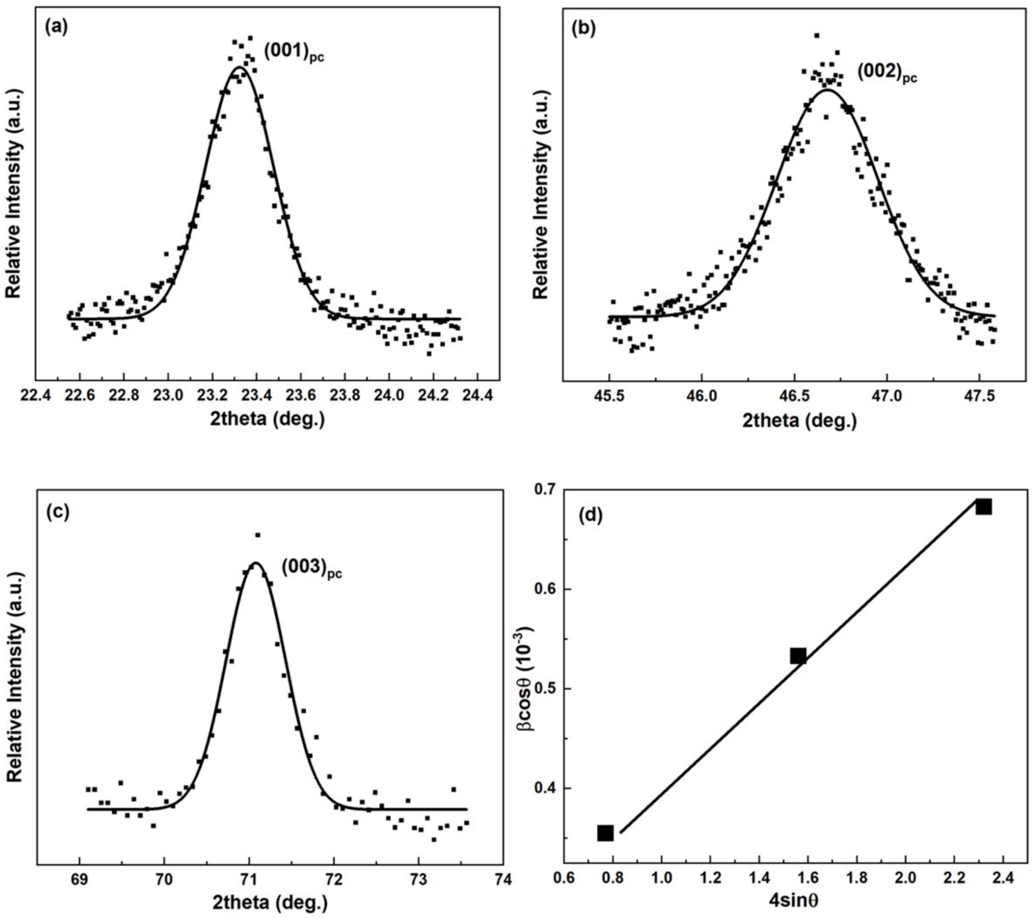

Figure S2 *XRD diffraction peaks of pseudo-cubic (a)* $(001)_{PC}$*, (b)* $(002)_{PC}$ *and (c)* $(003)_{PC}$ *of BSFNO-g thin film with 210nm thickness. (d) The fitting curves of Williamson Hall (W-H) diagram. The out of plane non-uniform strain (*u_i*) can be estimated by the slope of above linear fitting line.*