# Supplementary Information to

## Visible-light Photovoltaic effect in High-Temperature Ferroelectric $BaFe_4O_7$

**Ganghua Zhang,[*a,b] Jingshan Hou,[a] Mingjun Zhu,[b] Guoquan Huang,[b] Dezeng Li,[c] Yongzheng Fang[*a] and Tao Zeng[*b,d]**

[a]*School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai, 201418, P. R. China;*

[b]*Shanghai Key Laboratory of Engineering Materials Application and Evaluation, Shanghai Research Institute of Materials, Shanghai 200437, P. R. China;*

[c]*School of Chemistry and Molecular Engineering, East China Normal University, Shanghai, 200241, P.R. China;*

[d]*Advanced Science Research Laboratory, Saitama Institute of Technology, Okabe, Saitama 369-0293, Japan*

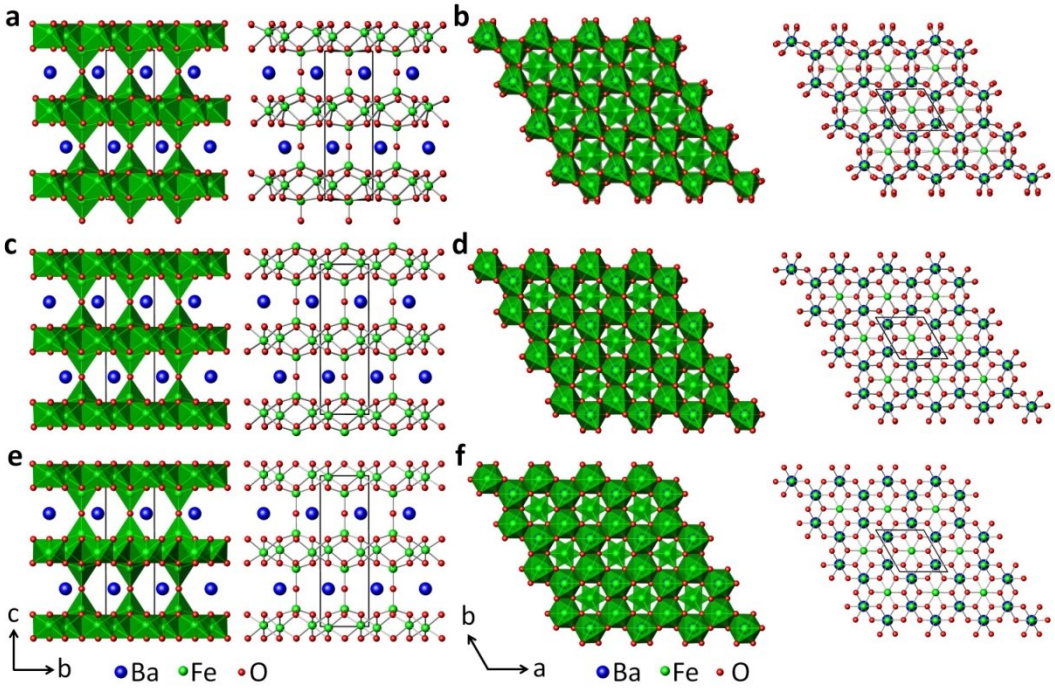


**Fig. S1**. Schematic polyhedral and ball-and-stick structure models of $BiFe_4O_7$ with space group $P3_1c$ (a,b), $P\text{-}3_1c$ (c,d) and $P6_3/m$ (e,f) viewed along *a* and *c*-axis, respectively.

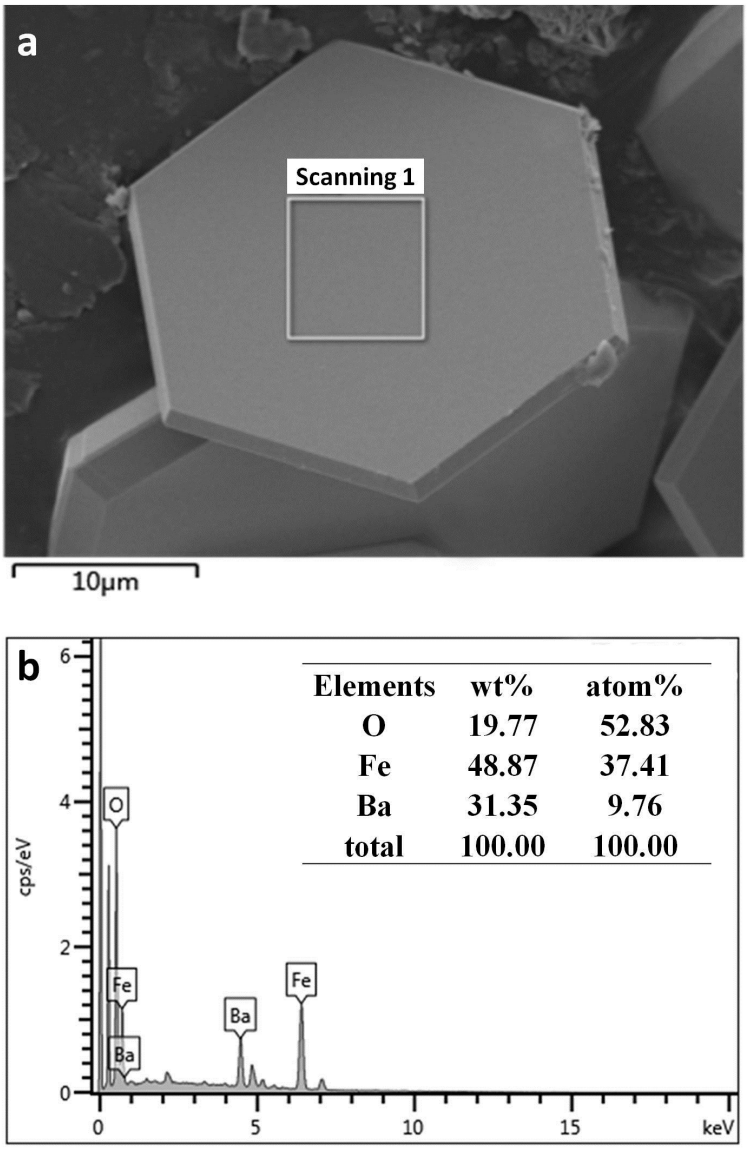


**Fig. S2.** SEM image and EDS analysis of $BaFe_4O_7$.

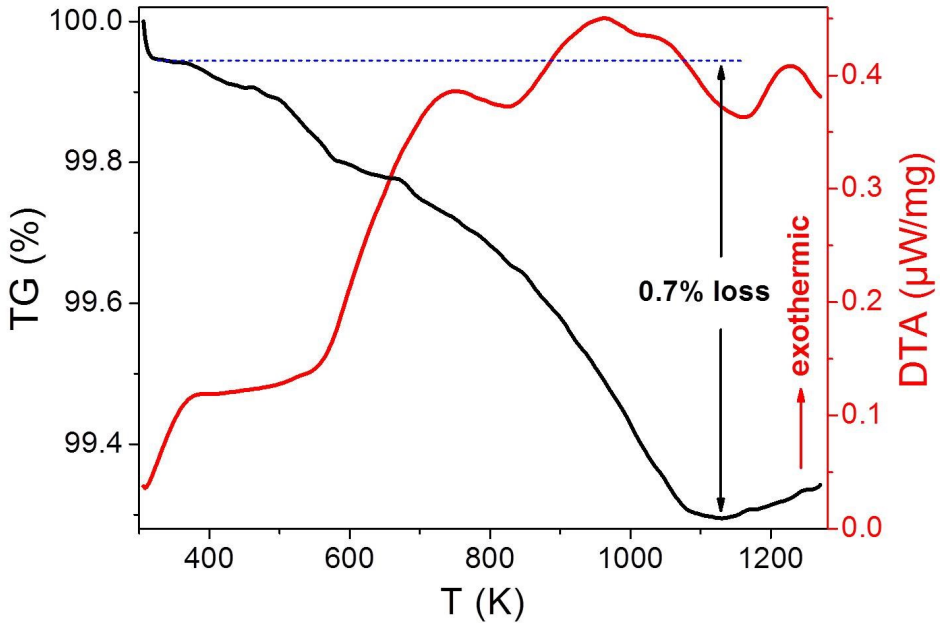


**Fig. S3.** TGA-DTA curves of $BaFe_4O_7$.

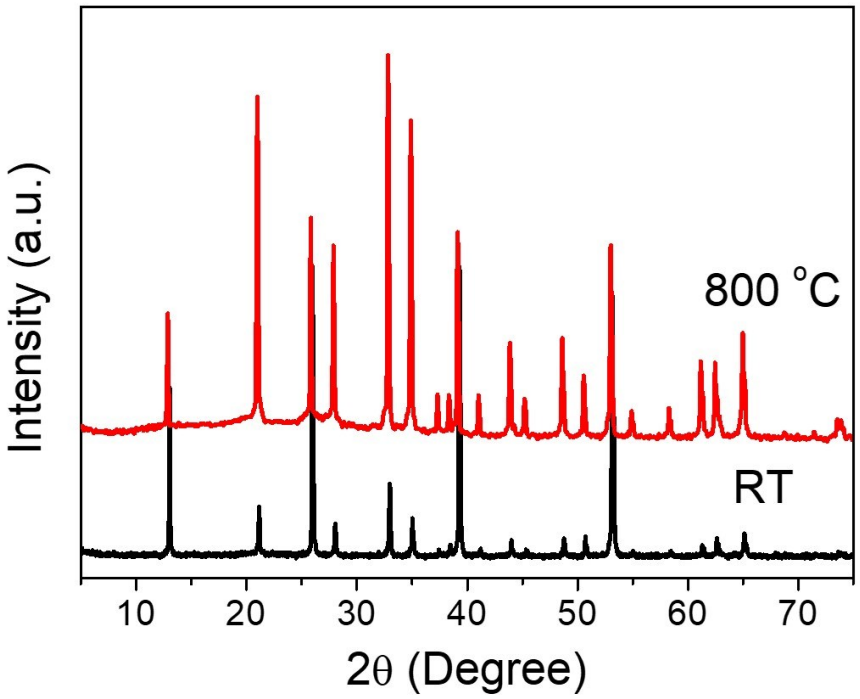


**Fig. S4.** The powder XRD of $BaFe_4O_7$ at room temperature (RT) and annealed at 800 $^oC$.

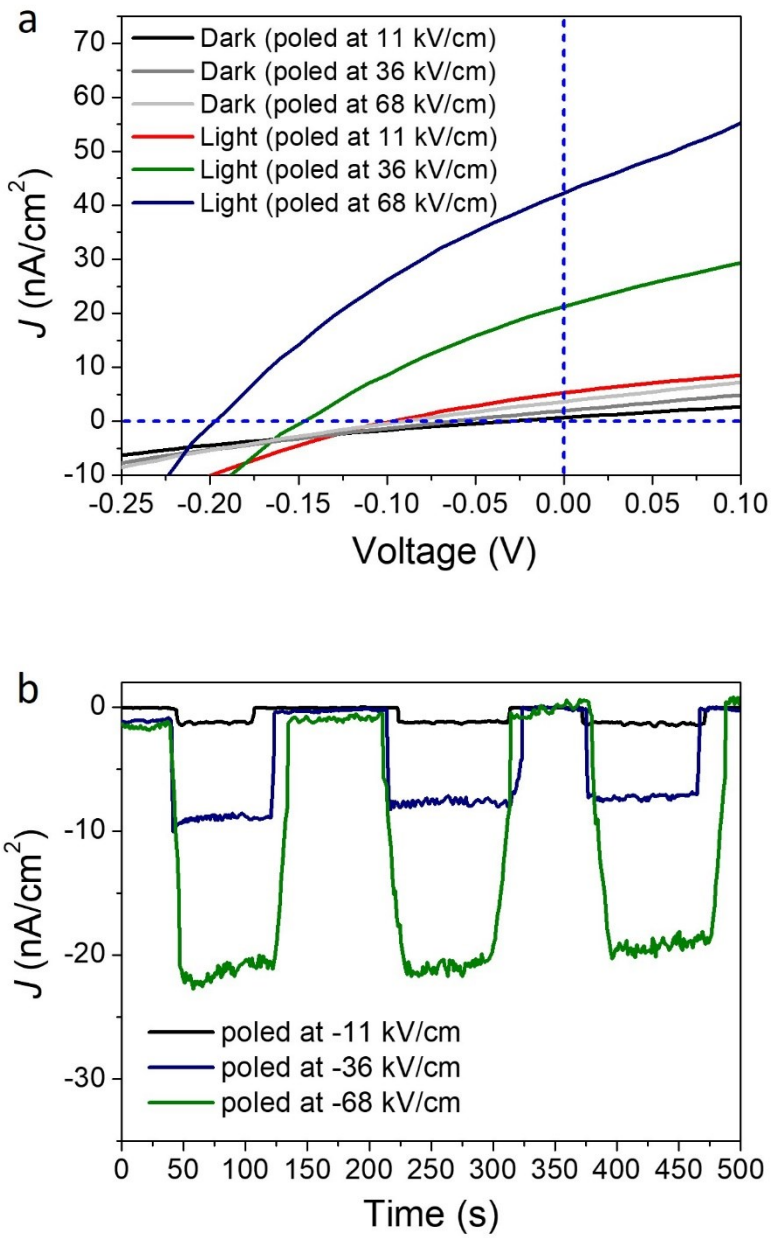


**Fig. S5.** (a) *J-V* curves of unpoled and poled ceramic samples in the dark and under visible-light illumination at room temperature. (b) Zero-bias photocurrent densities of negatively poled ceramic samples following on-off visible-light exposure.

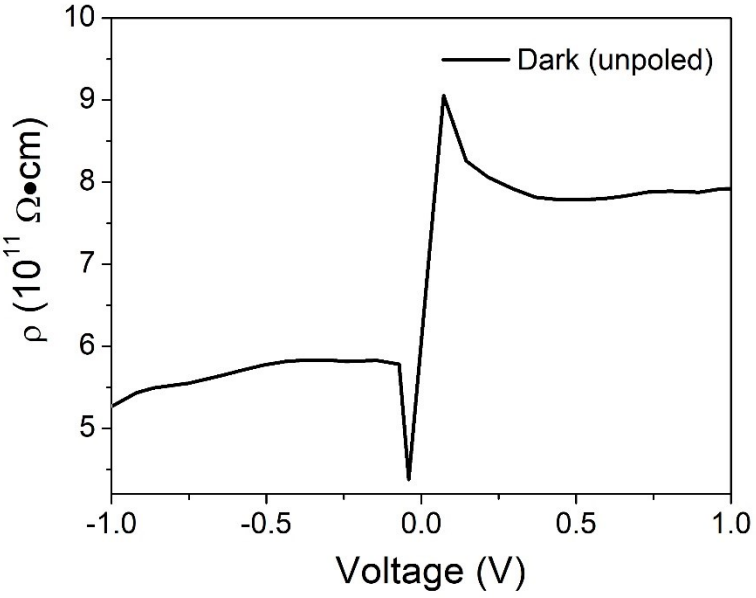


**Fig. S6.** The resistivity of $BaFe_4O_7$ calculated from *I-V* curve of the unpoled sample under dark condition according to Ohm's Law.

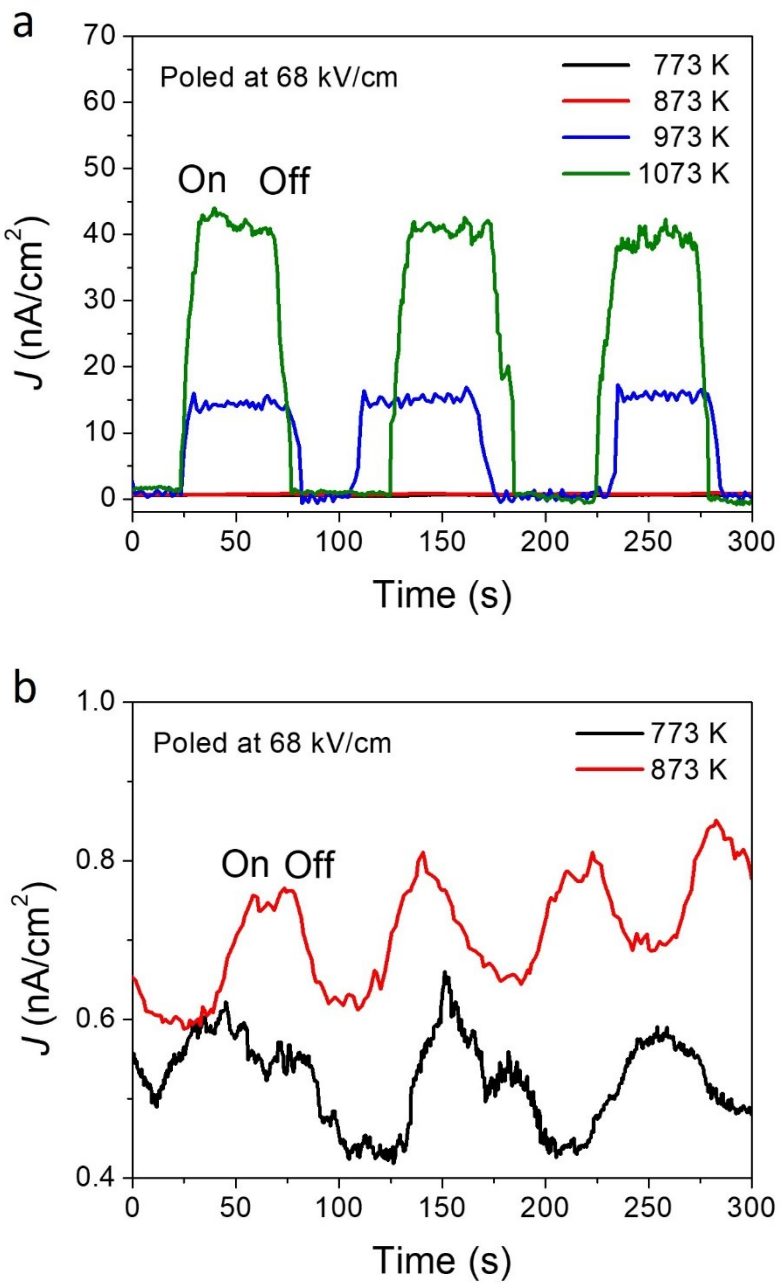


**Fig. S7.** (a) Zero-bias photocurrent densities of poled ceramic samples annealed at different temperatures following on-off visible-light exposure. (b) Enlarged view of zero-bias photocurrent curves of poled ceramic samples annealed at 773 and 873 K.

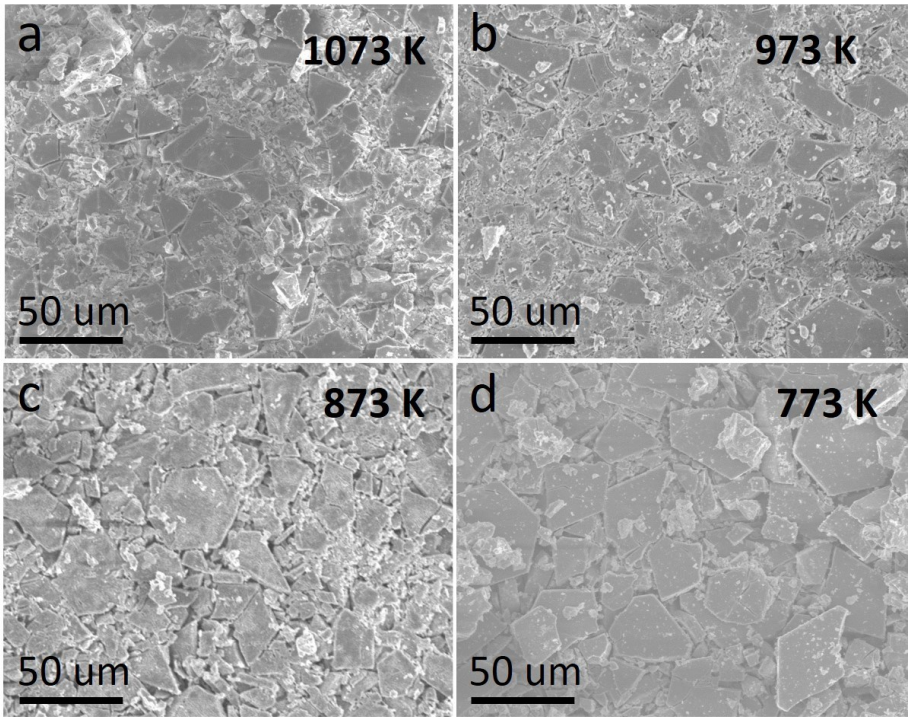


**Fig. S8.** SEM images of $BaFe_4O_7$ ceramic samples annealed at different temperatures.

**Table S1.** Refined structure parameters and selected bond lengths of $BaFe_4O_7$.[a]

| Space group | Agreement indices | Atoms | x | y | z | $U_{iso}$ (Å$^2$) | $g$ |
|---|---|---|---|---|---|---|---|
| $P3_1c$ | $R_{wp}$ = 5.97% | Ba | 0.6667 | 0.3333 | 0.3524(1) | 0.0194(2) | 1 |
| | $R_p$ = 3.63% | Fe1 | 0.0000 | 0.0000 | 0.2274(3) | 0.0137(1) | 1 |
| | $\chi^2$ = 1.57 | Fe2 | 0.0000 | 0.0000 | 0.4931(1) | 0.0061(1) | 1 |
| | | Fe3 | 0.3333 | 0.6667 | 0.1257(1) | 0.0113(1) | 1 |
| | | Fe4 | 0.3333 | 0.6667 | 0.5963(1) | 0.0075(1) | 1 |
| | | O1 | 0.4026(4) | 0.0306(1) | 0.1778(2) | 0.0477(1) | 1 |
| | | O2 | 0.0232(1) | 0.6193(1) | 0.5132(1) | 0.0553(1) | 1 |
| | | O3 | 0.0000 | 0.0000 | 0.3581(1) | 0.0236 (1) | 1 |
| $P\text{-}3_1c$ | $R_{wp}$ = 7.07% | Ba | 0.6667 | 0.3333 | 0.2500 | 0.0115(2) | 1 |
| | $R_p$ = 4.35% | Fe1 | 0.0000 | 0.0000 | 0.1159(3) | 0.0047(4) | 1 |
| | $\chi^2$ = 1.76 | Fe2 | 0.3333 | 0.6667 | 0.0087(1) | 0.0192(3) | 1 |
| | | O1 | 0.0000 | 0.0000 | 0.2500 | 0.0067(1) | 1 |
| | | O2 | 0.3556(2) | 0.0091(1) | 0.0818(1) | 0.0445(2) | 1 |
| $P6_3/m$ | $R_{wp}$ = 7.43% | Ba | 0.6667 | 0.3333 | 0.2500 | 0.0198(2) | 1 |
| | $R_p$ = 4.56% | Fe1 | 0.0000 | 0.0000 | 0.1149(4) | 0.0061(1) | 1 |
| | $\chi^2$ = 1.50 | Fe2 | 0.3333 | 0.6667 | 0.0089(1) | 0.0184(3) | 1 |
| | | O1 | 0.0000 | 0.0000 | 0.2500 | 0.0051(1) | 1 |
| | | O2 | 0.3435(1) | 0.3377(2) | 0.0790(1) | 0.0287(5) | 1 |

| | Selected bond length (Å) | | | |
|---|---|---|---|---|
| $P3_1c$ | Fe1—O1 | 2.114(12) | Fe1—O3 | 1.807(2) |
| | Fe2—O2 | 2.042(1) | Fe2—O3 | 1.865(11) |
| | Fe3—O1 | 1.869(5) | Fe3—O2 | 2.292(1) |
| | Fe4—O1 | 1.852(3) | Fe4—O2 | 1.881(1) |
| $P\text{-}3_1c$ | Fe1 —O1 | 1.855(1) | Fe1— O2 | 1.869(2) |
| | Fe2 —O2 | 1.986(3) | Fe2 —O2 | 2.061(2) |
| $P6_3/m$ | Fe1— O2 | 1.824(2) | Fe1 —O1 | 1.869(5) |
| | Fe2— O2 | 1.976(1) | Fe2 —O2 | 2.071(1) |

[a]Numbers in parentheses are standard deviations of the last significant digit. $U_{iso}$ is the isotropic thermal parameter, $g$ is the occupation factor. $R_{wp}$ and $R_p$ are agreement indices for the structure refinements by the Rietveld method. Cell parameters: $a = b$ = 5.153(1) Å, $c$ = 13.833(1) Å, $\alpha = \beta$ = 90°, $\gamma$ = 120° and $V$= 318.10(2) Å$^3$.