Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Ferroelectric Mesocrystalline $BaTiO_3/BaBi_4Ti_4O_{15}$ Nanocomposite: Formation Mechanism, Nanostructure, and Anomalous Ferroelectric Response

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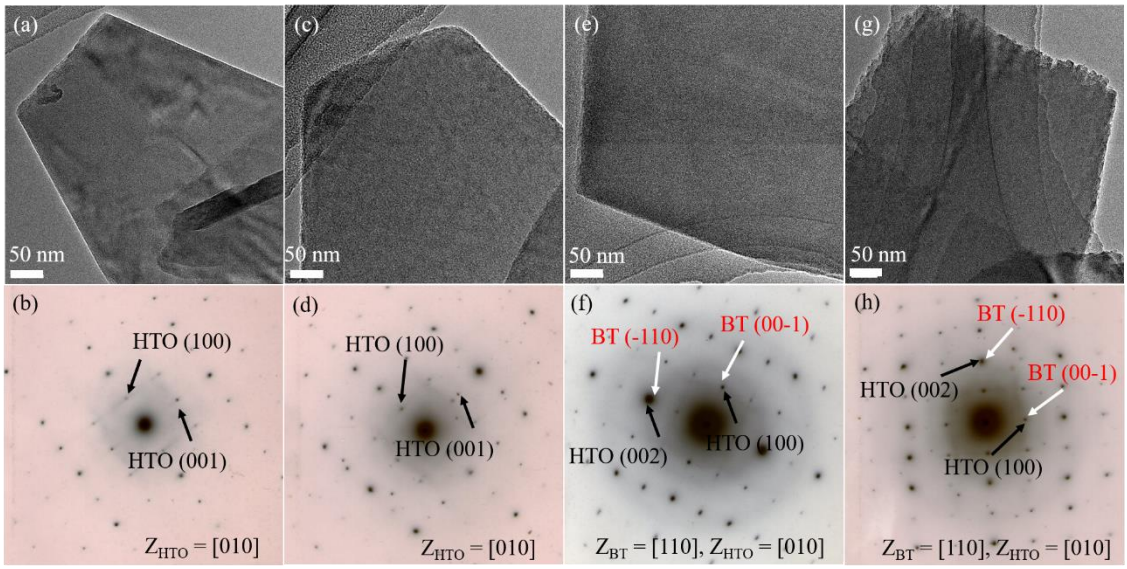

Figure. S1. (a, c, e, g) TEM images and (b, d, f, h) SAED patterns of (a, b) HTO, (c, d) BT/HTO-0.25, (e, f) BT/HTO-0.5 and (g, h) BT/HTO-0.75.

According to Figure. S1, it is obvious that all the samples exhibit the platelike morphology. HTO and BT/HTO-0.25 exhibit the SAED patterns of the single crystal of layered titanate with a [010] crystal-axis orientation. BT/HTO-0.5 and BT/HTO-0.75 exhibit the SAED patterns of mesocrystalline BT/HTO nanocomposite, where the single-crystal-like SAED patterns of BT and HTO are observed.

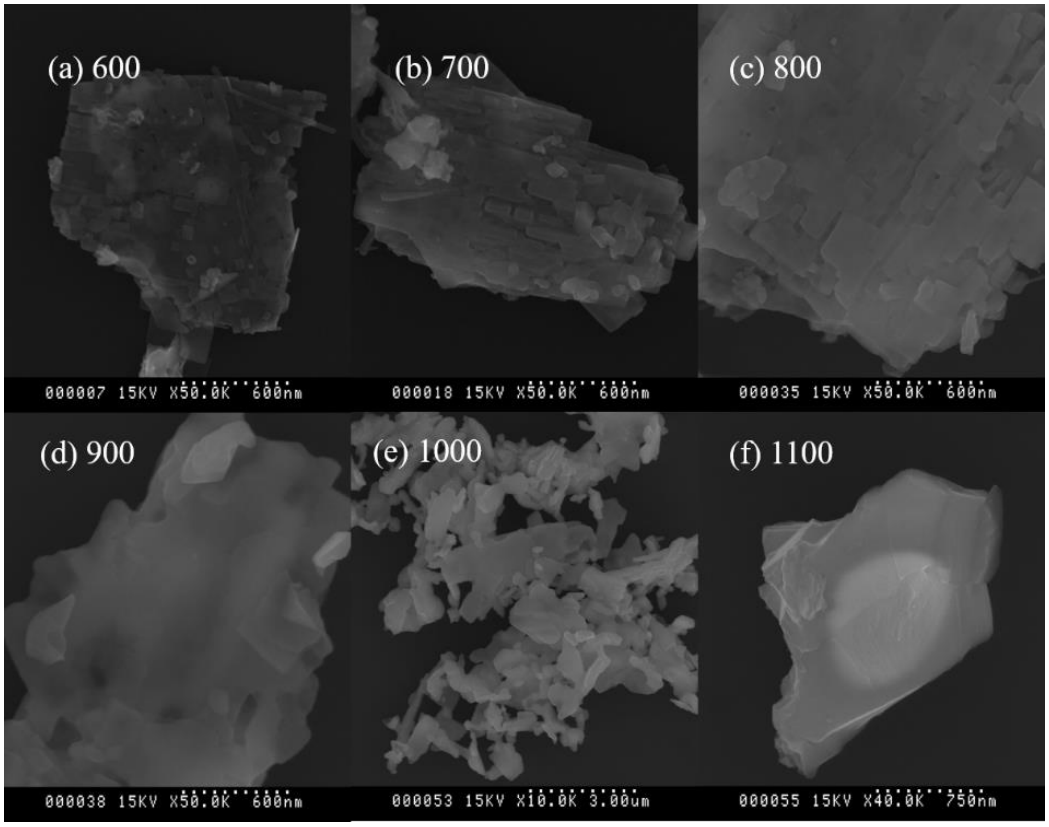

Figure. S2. FE-SEM images of the samples obtained by the heat-treatment of the (BT/HTO-0.5)-Bi_2O_3 mixture at different temperatures for 3 h.

The platelike particle morphology of the BT/HTO precursor are retained up to 900 ºC, and then destructed over 1000 ºC with increasing the heating temperature.

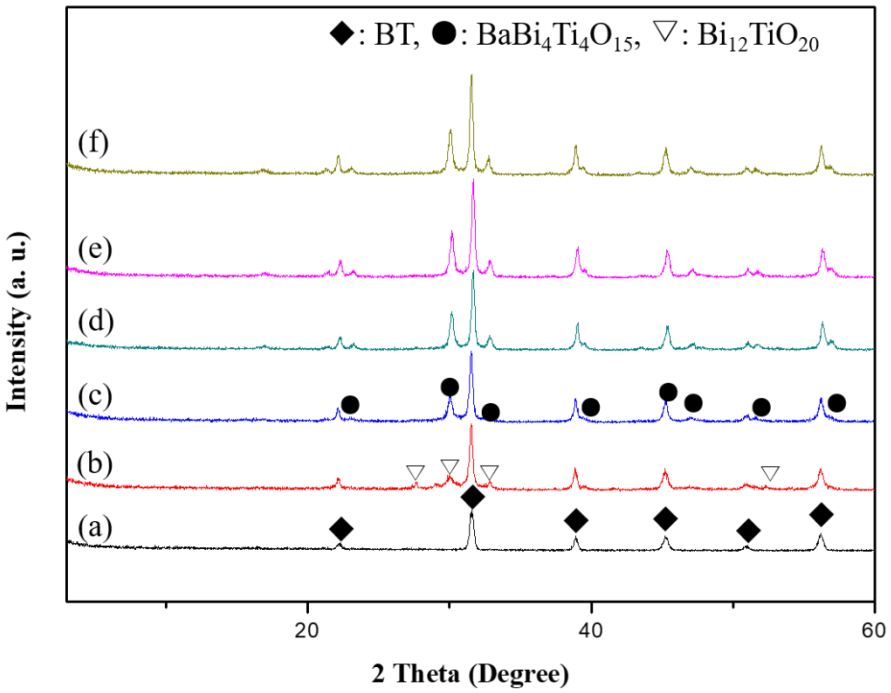

Figure. S3. XRD patterns of samples obtained by heat-treatments of (a) BT mesocrystal at 800 °C for 3 h and (BT/HTO-0.75)-Bi_2O_3 mixture at (b) 600, (c) 700, (d) 800 (e) 900 and (f) 1100 °C for 3 h.

Figure. S3 shows the XRD patterns of samples obtained by heat-treatment of BT mesocrystal at 800 °C for 3 h and (BT/HTO-0.75)-Bi_2O_3 mixture at different temperatures for 3 h. The formation of the BT phase can be clearly seen from the XRD result. In the (BT/HTO-0.75)-Bi_2O_3 reaction system, with increasing the heating temperature, the BT phase and a new phase of $Bi_{12}TiO_{20}$ were observed when the heating temperature reached 600 °C, the mixtures of BT and BBT phases were obtained in the temperature range above 700 °C.

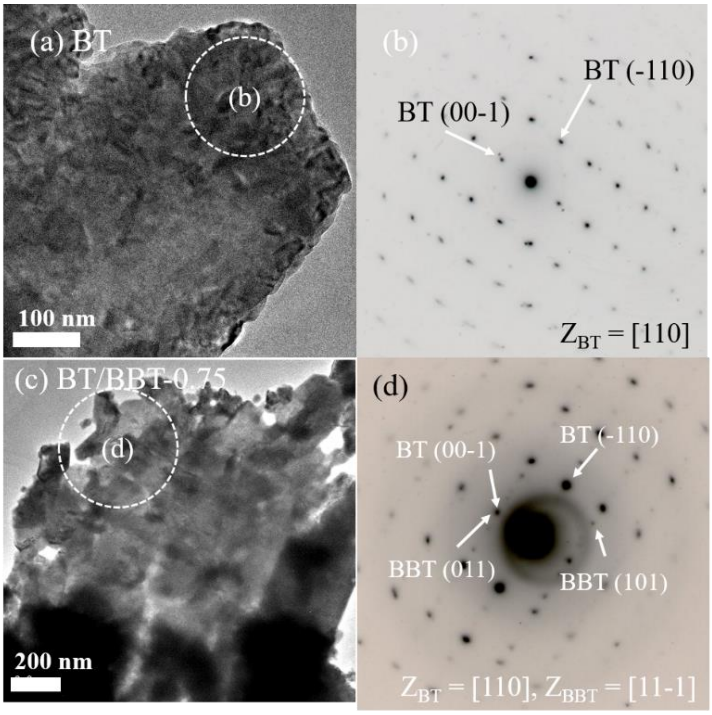

Figure. S4. (a, c) TEM images and (b, d) SAED spot patterns of samples obtained by heat-treatment of (a, b) the BT mesocrystal and (c, d) (BT/HTO-0.75)-Bi_2O_3 mixture at 800 °C for 3 h, respectively.

The platelike BT-800 particle is a polycrystal constructed from the BT nanocrystals, and each nanocrystals show the same crystal-axis orientation along the [110] direction, namely the formation of the BT mesocrystal. The platelike BT/BBT-0.75-800 sample also exhibits the platelike morphology. Two sets of SAED spots corresponding to BT and BBT can be observed simultaneously in one particle, namely BT/BBT-0.75 is a mesocrystalline BT/BBT nanocomposite.

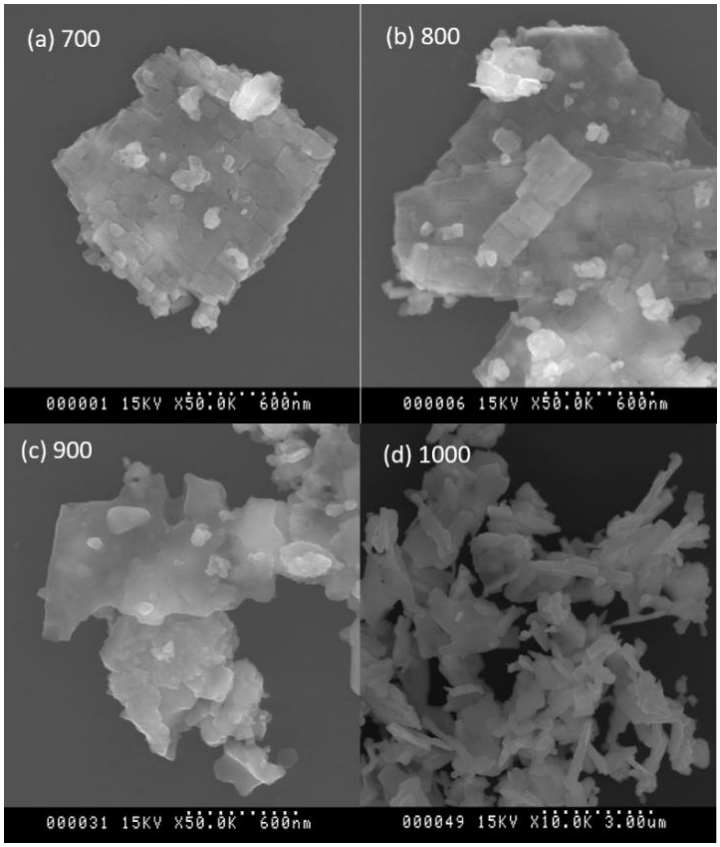

Figure. S5. FE-SEM images of samples obtained by heat-treatment of (BT/HTO-0.25)-Bi_2O_3 mixture at different temperatures for 3 h.

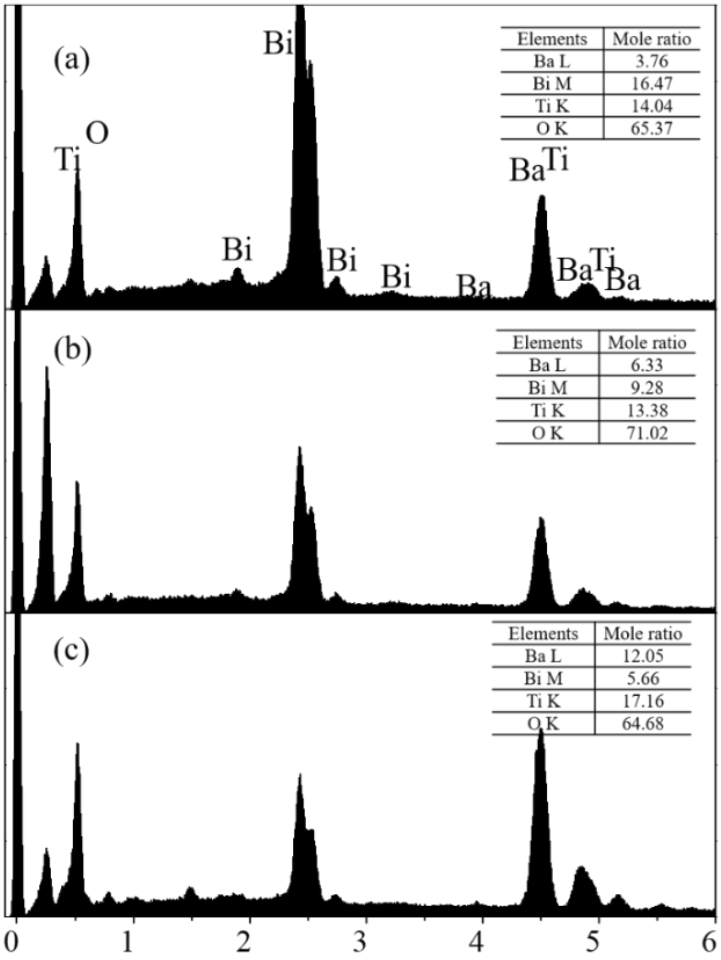

Figure. S6. SEM-EDS spectra for (a) BBT-1100, (b) BT/BBT-0.5-1100 and (c) BT/BBT-0.75-1100 samples.

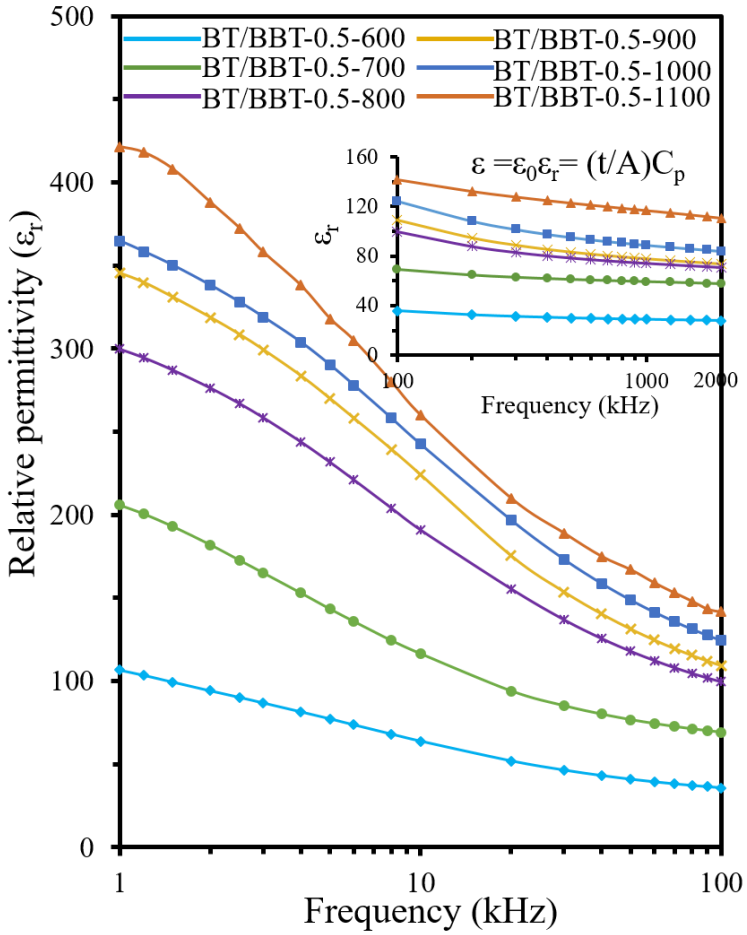

Figure. S7. Variations of relative permittivity (ε_r) with frequency for BT/BBT-0.5 samples obtained at different temperatures.

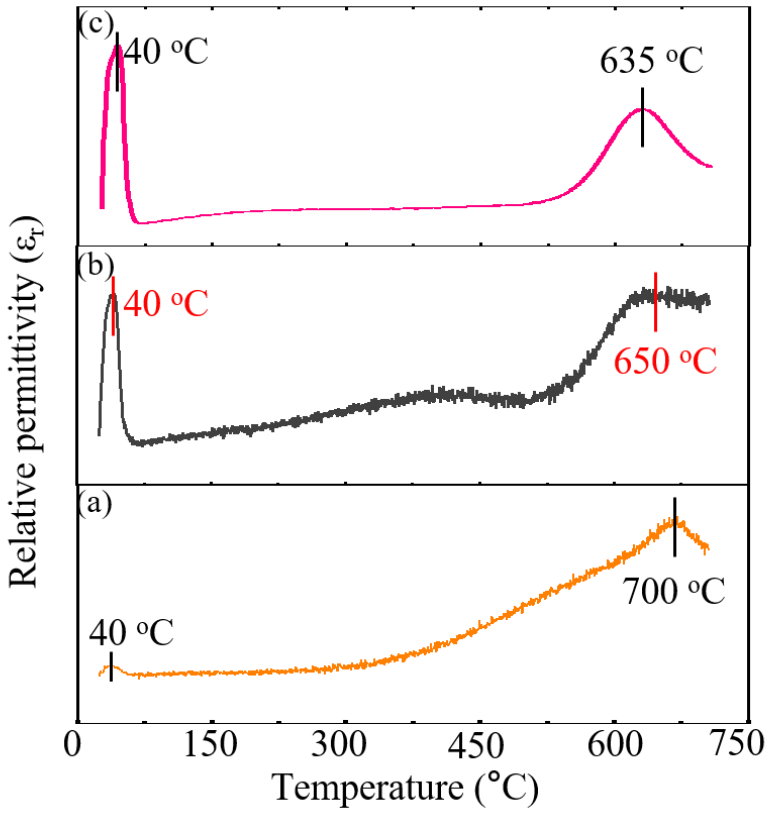

Figure. S8. Temperature dependences of relativie permittivities (ε_r) for (a) BT/BBT-0.5-800, (b) BT/BBT-0.5-900, and (c) BT/BBT-0.5-1100 at measurement frequency of 10 kHz.

Table S1. Sizes of BT nanocrystals in BT/BBT-0.5 nanocomposites obtained at different temperatures, and in BT/BBT-0.75-800 nanocomposite and BT-800 mesocrystal.

Sample	Size of BT nanocrystal*			
	800 °C	900 °C	1000 °C	1100 °C
BT/BBT-0.5	40 nm	50 nm	55 nm	70 nm
BT/BBT-0.75	70 nm	-	-	-
BT mesocrystal	75 nm	-	-	-

* Scherrer equation (also referred to as the Debye–Scherrer equation) was applied to estimate the sizes of BT nanocrystals in BT/BNT nanocomposites and BT mesocrystal, as shown followed:

$$D(2\theta)_{110} = K\lambda/(B\cos\theta_{110})$$

Where D is the average nanocrystal size, K is a constant (K = 0.89), λ is the wavelength of the X-ray source (λ = 0.154056 nm), B is the value of the full width at half maximum (FWHW) of the diffraction peak of plane (110) and θ is the Bragg angle.[1-2]

Reference

1. A. W. Burton, K. Ong, T. Rea and I. Y. Chan, *Microporous Mesoporous Mater.*, 2009, **117**, 75-90.

2. J. S. J. Hargreaves, *Catalysis, Structure & Reactivity*, 2016, **2**, 33-37.