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Supporting information:

Topochemical transformation of single crystalline $SrTiO_3$ microplatelets from $Bi_4Ti_3O_{12}$ precursors and their orientation dependent surface piezoelectricity

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Experimental procedure

A novel synthesis route was designed to produce perovskite $SrTiO_3$ microplatelets by topochemical conversion (TMC) from Aurivillius $Bi_4Ti_3O_{12}$ precursors. Firstly, $Bi_4Ti_3O_{12}$ precursors were prepared by molten salt synthesis according to the following reaction:

$$2Bi_2O_3+3TiO_2 \rightarrow Bi_4Ti_3O_{12} \quad (1)$$

During this step, analytical grade Bi_2O_3 and TiO_2 powders were mixed in a stoichiometric molar ratio of 2:3 by ball-milling in ethanol for 12 h, and then an equal weight of NaCl-KCl salts (1:1 molar ratio) were added to the mixture by ball-milling for another 12 h. The dried powder mixture was heated at 1100 ℃ for 1 h in an alumina crucible. The product was washed several times with hot deionized water to remove salts. Next, using the platelike $Bi_4Ti_3O_{12}$ precursors, the topochemical conversion of $SrTiO_3$ microplatelets was carried out in accordance with the following reaction:

$$Bi_4Ti_3O_{12}+3SrCO_3 \rightarrow 3SrTiO_3+2Bi_2O_3+3CO_2 \quad (2)$$

In this step, $Bi_4Ti_3O_{12}$ precursor particles and $SrCO_3$ powder were mixed in a molar ratio of 1:4.5, and then an equal weight of KCl salt was added. Here 50 wt% excess $SrCO_3$ reactant was used to facilitate the thoroughly compositional/structural conversion from $Bi_4Ti_3O_{12}$ to $SrTiO_3$. In order to investigate temperature-driven structural, morphological and interfacial evolutions during this conversion process, the dried powder mixtures were respectively heated at 5 ℃/min to between 600 and 1100 ℃, and then immediately air-quenched. The quenched samples were gently soaked in deionized water to remove salt, without significantly damaging their fine morphology features. Afterward, a large batch of powder mixture was heated at 1100 ℃ for 3 h, and then the KCl salt, unreacted $SrCO_3$, and Bi_2O_3 byproduct were removed by washing with deionized water and soaking in 30% HNO_3, respectively. Finally, the synthesized $SrTiO_3$ microplatelets were dispersed by ultrasonicating and rinsed 5 times with deionized water. It should be noted that 1100 ℃ is an optimized temperature to produce high-quality $SrTiO_3$ microcrystals, but not the minimum temperature.

Phase purity and crystal structure/orientation were analyzed by X-ray diffraction (XRD, D/max 2400, Rigaku, Tokyo, Japan). For structure evolution analysis, quenched samples were ground in a mortar and pestle to minimize the preferred orientation, and then the total XRD peak intensity for each phase of interest was calculated by profile fitting only the relevant peaks in each data set, after subtracting background. To complement the XRD analysis on structure transformation, differential thermal analysis (DTA) was performed using Thermoanalyzer Systems (Q600SDT, TA Instruments, USA). Raman scattering spectra were recorded at room temperature with a LabRAM XploRA spectrometer (HORIBA Jobin Yvon S.A.S., France). Morphological and compositional features were observed using field-emission scanning electron microscopy (FE-SEM, Helios NanoLab 600i, FEI, OR, USA) combined with energy-dispersive X-ray spectrometry (EDS). To study morphological/ structural/interfacial evolutions at a finer scale, the cross-sections of the converting samples were obtained via focused ion beam (FIB, Helios NanoLab 600i), and then observed via a field-emission gun transmission electron microscopy (FEG-TEM, Talos F200X, FEI). The height/amplitude/phase images and local electrical responses (phase-voltage hysteresis loop and amplitude-voltage butterfly curve) of the synthesized $SrTiO_3$ microplatelets were recorded by piezoelectric force microscopy (PFM, MFP-3D, Asylum Research, USA). Because the large side lengths (~11–16 μm) of $SrTiO_3$ microplatelets restrict the local PFM electrical measurements perpendicular to [001], smaller pieces with one side length ~3-5 μm were cut and used for the phase-voltage hysteresis loop and amplitude-voltage butterfly curve tests.