

Supporting information:

Topochemical transformation of single crystalline SrTiO₃ microplatelets from Bi₄Ti₃O₁₂ precursors and their orientation dependent surface piezoelectricity

Jie Wu¹, Yunfei Chang^{1*}, Weiming Lv¹, Guicheng Jiang¹, Yuan Sun¹, Yingchun Liu¹, Shantao Zhang², Bin Yang^{1*}, Wenwu Cao^{1,3}

¹Condensed Matter Science and Technology Institute, School of Science, Harbin Institute of Technology, Harbin 150080, China

²National Laboratory of Solid State Microstructures and Department of Materials Science and Engineering, Nanjing University, Nanjing 210093, China

³Materials Research Institute and Department of Mathematics, The Pennsylvania State University, University Park, PA 16802, USA

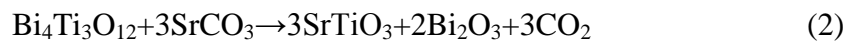
* Corresponding author. Email address: changyunfei@hit.edu.cn (Y. Chang), binyang@hit.edu.cn (B. Yang)

Experimental procedure

A novel synthesis route was designed to produce perovskite SrTiO₃ microplatelets by topochemical conversion (TMC) from Aurivillius Bi₄Ti₃O₁₂ precursors. Firstly, Bi₄Ti₃O₁₂ precursors were prepared by molten salt synthesis according to the following reaction:



During this step, analytical grade Bi₂O₃ and TiO₂ 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 °C for 1 h in an alumina crucible. The product was washed several times with hot deionized water to remove salts. Next, using the platelike Bi₄Ti₃O₁₂ precursors, the topochemical conversion of SrTiO₃ microplatelets was carried out in accordance with the following reaction:



In this step, Bi₄Ti₃O₁₂ precursor particles and SrCO₃ 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 SrCO₃ reactant was used to facilitate the thoroughly compositional/structural conversion from Bi₄Ti₃O₁₂ to SrTiO₃. In order to investigate temperature-driven structural, morphological and interfacial evolutions during this conversion process, the dried powder mixtures were respectively heated at 5 °C/min to between 600 and 1100 °C, 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 °C for 3 h, and then the KCl salt, unreacted SrCO₃, and Bi₂O₃ byproduct were removed by washing with deionized water and soaking in 30% HNO₃, respectively. Finally, the synthesized SrTiO₃ microplatelets were dispersed by ultrasonication and rinsed 5 times with deionized water. It should be noted that 1100 °C is an optimized temperature to produce high-quality SrTiO₃ 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 SrTiO₃ microplatelets were recorded by piezoelectric force microscopy (PFM, MFP-3D, Asylum Research, USA). Because the large side lengths (~11–16 μm) of SrTiO₃ 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.