

Editorial

Environmental Friendly High Performance Ferroelectric Materials from Earth Abundant Elements

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Since the discovery of ferroelectricity in 1920 by Valasek, ferroelectric (FE) materials have been widely investigated due to their spontaneous charge polarization, and piezoelectricity [1,2]. Typically FE perovskite oxide materials exhibit long range alignment of electric dipoles resulting in a net polarization under an applied electric field [1,2]. The unit cell of a FE crystal has a polar axis that causes spontaneous electric dipole moment even when the electric field is withdrawn [1]. Due to this property and other characteristics such as pyroelectricity and large dielectric constants, FE materials are potential components in a wide spectrum of applications such as nonvolatile random access memories, high frequency electrical components, portable data devices and micro-electro-mechanical devices.³ They are also being explored for various sensor and actuator applications as high-frequency electrical components and tunable microwave circuits [3].

Among the classical perovskite oxide materials, $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PZT) has been extensively studied for its high FE polarization and piezoelectric coefficient [4]. However the use of toxic Pb in FE devices and the consequential environmental concerns have resulted in efforts to find novel environmental-friendly FE materials with comparable or even better polarization properties as compared to PZT. As alternative choice, an increased interest is around the Non-centrosymmetric (NCS) complex oxides based one or more of earth abundant non-toxic elements (K, Zn, Sn, Ti, Ba and Ca). Due to the symmetry-dependent FE properties, key focus is particularly on LiNbO_3 (LN)-type NCS compounds which are polar structural derivatives of their perovskite counterparts [5]. Theoretical calculations indicate that unlike perovskites, the cooperative cation shift along the c-axis direction against close-packed anions in LN-type compounds results in higher spontaneous polarization and therefore may hold great potential as non-toxic replacements for current Pb-based FE materials [5].

However, despite high theoretical promises, experimental studies on the growth, stability and properties of functional LN-type oxides have been limited compared to the typical Pb-based state-of-the-art perovskite oxides, mainly due to the difficulty in synthesizing these metastable phases by traditional solid state synthesis processes under ambient conditions. This is partly related to the disproportionation of low-valence coordination to higher valence ionic and metallic states

to form its typical hexagonal symmetry LN-type lattice. An enhanced covalence qualifies these electronic structures as it was inferred from analyzing the chemical bonding.

A significant achievement towards this end has been realized for the first time by our group. We opted for a novel hybridphysical/chemical approach encompassing Pulsed Laser Deposition (PLD) and solvothermal process for growing vertically aligned LN-type nanostructure arrays on industrially viable substrates [6]. In this process, initially a ≤ 100 nm thick seed-layers of template material was deposit with identical crystal symmetry and minimum lattice mismatch between the LN-type material and the template material using PLD process. The nucleation and growth of metastable LN-type materials in nanostructured form was facilitated through the stabilization of the required phase in energetically favorable chemical environment under auto-generated pressurized solvothermal approach. We observed that the down-scaling size effects played an effective role in stabilizing the metastable FE LN-type phases such as observed in ZnSnO_3 (Scheme shown in Figure 1). Vertically aligned and highly packed (≥ 0.8) LN-type ZnSnO_3 nanowire (NW) arrays of ≈ 20 μm was successfully grown by this approach through lattice masking on oriented ZnO: Al nano crystalline template seed-layer that also served as bottom-electrode during the construction of FE capacitive device (Figure 1). The high density of the nanostructured thick filmson conducting substrates was largely achieved due to unique 'welding' process that joins the adjacent ZnSnO_3 NWs.

The performance of this integrated FE device based on oriented nanostructured thick films therefore was possible to determine as-is without using polymeric filler that showed a superior polarization value as high as $38 \mu\text{C}/\text{cm}^2$ as compared to $\approx 30 \mu\text{C}/\text{cm}^2$ in PZT ceramics [6]. This finding, employed by the simple, cost-effective, and industrially scalable technology suggests that we might find attractive functional properties by the selection of other polar LN-type perovskites, also conducive for FE applications. As a newly emerging and highly interdisciplinary field, the progress in the successful growth, integration of devices and FE measurements of LN-type nanostructures is critical and this work will open new pathways for fabrication of future FE devices based on these technologically important materials.

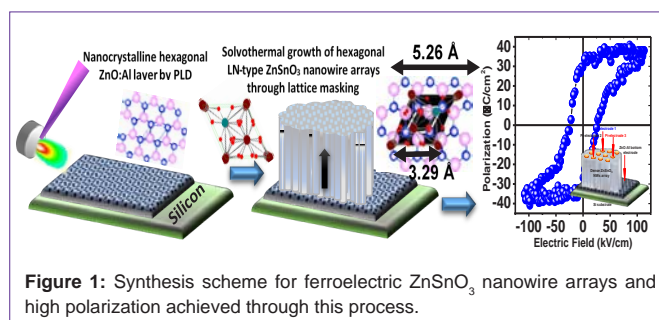


Figure 1: Synthesis scheme for ferroelectric ZnSnO_3 nanowire arrays and high polarization achieved through this process.

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