

New Route to Design Vertically Aligned Multiferroic Nanocomposites

S. Basov^{1,2}, C. Elissalde¹, and L. Piraux^{2,*}

¹ ICMCB-CNRS, Université de Bordeaux

87 Avenue du Docteur Schweitzer, Pessac, France, 33600

² BSMA-IMCN, Université catholique de Louvain

1 Place Croix du Sud, Louvain-la-Neuve, Belgium, 1348

*Sergey Basov: sergey.basov@uclouvain.be

Multiferroic materials have been intensively studied due to the promising coupling of ferroelectricity, ferromagnetism and ferroelasticity in one material leading to a wide range of multifunctional devices, such as memories, sensors, detectors, and microwave devices. The magnetoelectric effect (ME), which is the induction of the polarization by an applied magnetic field (direct ME effect) or the magnetization reversal by an applied electric field (converse ME effect), can be observed in two-phase multiferroic nanocomposites at room temperature through interface and strain interaction. Materials with strong piezoelectric $\text{Pb}_{0.52}\text{Zr}_{0.48}\text{TiO}_3$ (PZT), BaTiO_3 (BTO) and magnetostrictive properties CoFe_2O_4 (CFO) have been intensively studied in multilayered thin films. However, the strain in the multilayered nanostructures is limited due to the substrate-imposed clamping effect, and correspondingly the ME coupling is small. Therefore, designing innovative architectures is a challenge in the field of multiferroic nanocomposites. Strong ME coupling and reduced clamping effect has been demonstrated in multiferroic nanostructures with 1-3 connectivity, consisted of vertically aligned nanopillars (1) embedded into a matrix (3). In order to use the vertically aligned nanocomposites in device applications, it is necessary to control geometry, ordering, and density of the pillars.

In this work, we have developed new strategies for the preparation of 1-3 multiferroic nanocomposites. Two kinds of materials were considered: i) vertically aligned CFO nanopillar arrays embedded in a matrix ($\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ (BSTO), BTO, and PZT); ii) 3-D interconnected self-supported CFO nanowire networks embedded in a PZT matrix. In the first experiment, the deposition onto supported vertically aligned CoFe_2 nanopillar arrays of the ferroelectric BSTO and BTO layers is performed by rf magnetron sputtering, and the impregnation of the PZT matrix is made using sol-gel technique. The CoFe_2 nanopillars oxidation is conducted in-situ during sputtering or sol-gel processes. Figures 1 (a-c) and (d-f) illustrate schematic preparation of the vertical BSTO-CFO and 3-D PZT-CFO multiferroic nanocomposites. The efficiency and flexibility of a sol-gel technique have been previously demonstrated in the case of Ni@BTO and CFO@PZT nanocable arrays.^{1,2}

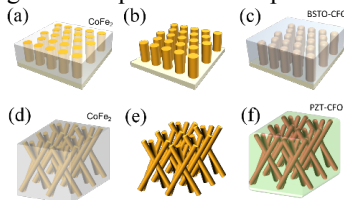


Figure 1. Preparation process of the nanocomposites with two geometries: (a) vertically aligned CoFe_2 nanopillar arrays obtained by electrodeposition into the vertical AAO nanoporous structure; (b) free-standing CoFe_2 nanopillar arrays obtained after dissolution of the template; (c) vertically aligned BSTO-CFO multiferroic nanocomposite made by deposition of the BSTO layer using magnetron sputtering and nanopillars simultaneous oxidation; (d) 3-D CoFe_2 nanowire networks in the polycarbonate templates; (e) self-supported CoFe_2 nanowire networks obtained after dissolution of the template; (f) 3-D PZT-CFO nanocomposite made by sol-gel impregnation of the PZT matrix and nanopillars simultaneous oxidation

The microstructural and morphological evaluations of nanocomposites include XRD, HRSEM and HRTEM characterizations. For magnetic and dielectric measurements, an alternating gradient magnetometry and impedance spectroscopy are utilized. The ME coefficient is determined as a function of DC magnetic field and temperature using adjusted Quantum Design physical property measurement system. The samples are mounted in longitudinal geometry, i.e. ME voltage is parallel to the direction of AC and DC magnetic fields.

Two types of two-phases multiferroic nanocomposites have been prepared. The magnetoelectric coupling in the vertically aligned CFO nanopillar arrays embedded inside the BSTO matrix have been observed and can be interpreted by ferroelectricity and ferrimagnetism of the two phases, along with the reduced clamping effect, which can enhance the strain interaction.

¹D. Sallagoity, et al., J. Mater. Chem. C **3**, 107 (2015)

²D. Sallagoity, et al., RCS Adv. **6**, 106716 (-2016)