Response to “Comment on ‘On the strain coupling across vertical interfaces of switchable BiFeO₃–CoFe₂O₄ multiferroic nanostructures’ ” [Appl. Phys. Lett. 96, 076101 (2010)]

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In our letter¹ we reported on the residual lattice strain in epitaxial BiFeO₃–CoFe₂O₄ (BFO–CFO) multiferroic nanostructures on SrTiO₃(001) (STO) substrates. The in-plane and out-of-plane parameters of CFO were relaxed and compressively strained, respectively. In the case of BFO, there was coexistence of relaxed (bulk lattice parameters) and epitaxially strained material. After chemical treatment we observed that the x-ray diffracted intensity of the strained and relaxed BFO were reduced or no longer visible, thus indicating that these distinct BFO phases were, respectively, partially and totally removed. This removal did not cause modification in the out-of-plane strain of CFO. Therefore, we concluded that the observed cell parameters of the CFO in the nanocomposites were not modified by epitaxial elastic interaction due to neighboring BFO component. We argued that the absence of residual elastic strain between CFO and BFO does not preclude the observed magnetoelectric coupling which is basically mediated by magnetostriction and piezoresponse of the nanocomposites under external stimuli.

Zhang *et al.*² consider in their comment that the out-of-plane strain of CFO in our samples is of elastic origin, and proposed that the strained BFO phase is located closer to the BFO–CFO interface, and that the tensile stress applied by CFO elongates the out-of-plane lattice of BFO, and that at the same time the very thin lateral BFO layer is tensile strained in the out-of-plane direction by CFO.

X-ray diffraction (XRD) reciprocal space maps and high-resolution transmission electron microscopy characterizations reported in Fig. 1 of our letter¹ show that the out-of-plane strained BFO presents an in-plane parameter fully strained by the STO substrate. This strongly supports the conclusion that the epitaxial stress induced by the substrate causes the BFO out-of-plane strain in our samples, thus constituting the experimental basis for our claim.

On the other hand, if one would accept the hypothesis of Zhang *et al.*, then it should be expected that the amount of strained BFO in nanocomposite films increases with thickness (*t*) due to the increase in the BFO–CFO interface area. We included in Fig. 1(e) of Ref. 1 the XRD θ – 2θ scan of a *t*=200 nm thick sample. Other three samples were prepared

in the same run of depositions changing only the growth time to obtain *t*=10, 50, and 100 nm thick samples. Here, the XRD θ – 2θ scans of the four samples are shown in Fig. 1(a). It is clear that the CFO(004) diffraction peak increases in intensity with thickness. The BFO(002) reflection shows only strained material in the thinnest samples and, interestingly, the intensity of this reflection does not change appreciably when the thickness increases. In contrast, the peak corresponding to relaxed BFO emerges and increases in intensity with thickness. The results presented in Fig. 1(a) do not support the spatial distribution suggested by Zhang *et al.*²

Zhang *et al.*² also stated that even if BFO had been completely removed after etching, CFO could remain strained in a metastable state due to an energy barrier between the strained and relaxed CFO. If this was the case an annealing of the sample would favor the relaxation of CFO. To investigate it, the etched sample was annealed for 3 h in air at various temperatures up to 500 °C, at which BFO is still stable.³ XRD θ – 2θ scans of the etched sample before and after the annealing at 500 °C [Fig. 1(b)] show no change in the peak positions of both CFO and BFO reflections. This observation points to an equilibrium “strained” state of CFO rather than a metastable one.

FIG. 1. (Color online) (a) XRD θ – 2θ scans of *t*=10, 50, 100, and 200 nm nanocomposites. S and R indicate strained and relaxed BFO, respectively. Vertical lines mark the positions of CFO(004) and BFO(002) in bulk materials. (b) XRD θ – 2θ scans of etched BFO–CFO sample before (red curve) and after annealing (500 °C, 3 h) in air (blue curve). Dotted line marks the position of CFO(004) in bulk material.

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Finally, we like to emphasize that the absence of *residual* elastic strain does not imply absence of elastic coupling at the CFO-BFO interface, and indeed we conclude in Ref. [1](#) that the two phases couple are mechanically effective enough for experimental confirmation of magnetoelectric coupling.

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