Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.


# Supplementary Information for Enhancement of phase stability and optoelectronic performance of $BiFeO_3$ thin films via cation co-substitution

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## 1 Ionic radii

Table S1 Ionic radii of A-site and B-site cations in BFO [1,2]

| Cation | $r_i$ () A-site NC=12 | $r_i$ () B-site NC=6 |
|---|---|---|
| $Bi^{3+}$ | 1.54 | |
| $La^{3+}$ | 1.36 | |
| $Fe^{3+}$ | | 0.55 LS/0.65 HS |
| $Co^{3+}$ | | 0.55 LS/0.61 HS |
| $Co^{2+}$ | | 0.65 LS/0.75 HS |

*LS= low spin HS= high spin

Note that the ionic radii of $Bi^{3+}$ in NC=12 is not tabulated in Shannon *et al.*.[1] For consistency, it has been included an estimated value for NC=12 although it might be overestimated.[2]

## 2 Surface morphology by AFM

The influence of La substitution on the surface morphology is shown in Fig. S1. AFM topographic images reveal that the films present an homogeneous and dense surface with an root mean square (rms) roughness of ∼ 1 - 2 nm. With the incorporation of La, the surface morphology is at least as good as BFCO films with low rms roughness. Smooth and homogeneous surface is desired to fabricate a multilayered device architecture.

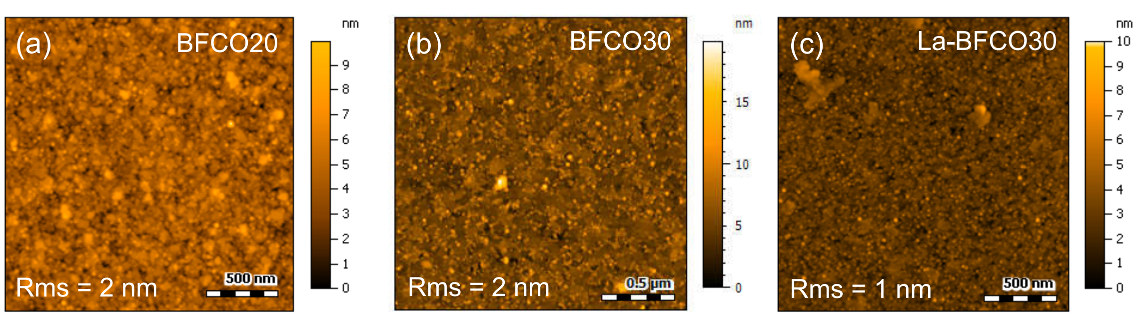


Fig. S1 5$\mu$m x 5 $\mu$m topographic AFM images of (a) BFO, (b) BFCO30 and (c) La-BFCO30 films on STO.

## 3 Optical Constants by SE

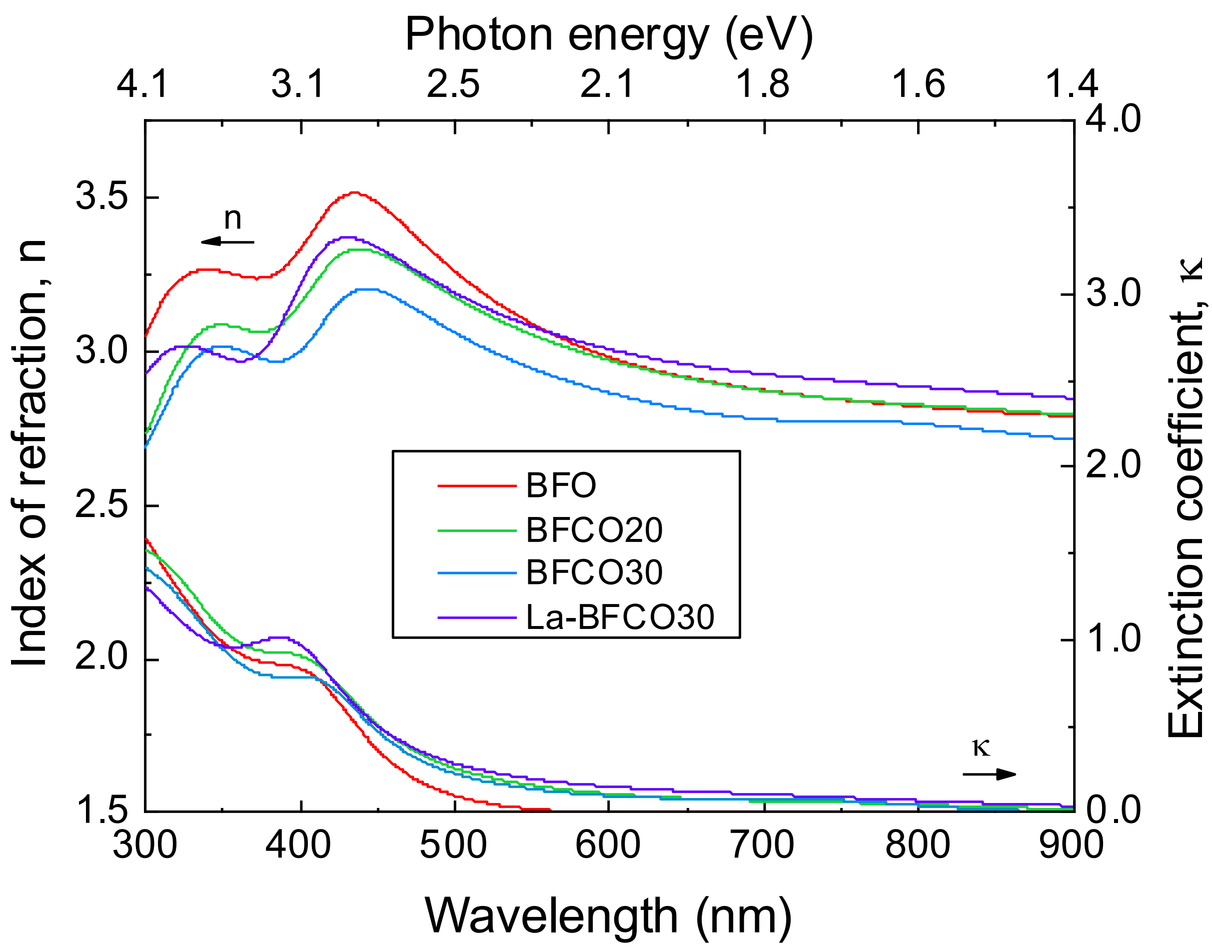


Fig. S2 n and k optical constants of 20 nm (a) BFCO30 and (b) La-BFCO30 films on STO substrates extracted from spectroscopic ellipsometry measurements.

## 4 Valence Band

The peaks in the binding energy range of 3 eV - 10 eV are due to O 2p, Fe 3d and Bi 6s occupied states, while the peak near the valence band maximum, in the range 1 eV - 3 eV is due to the $Co^{2+}$ occupied states, Fig. S3. The shape of the valence band spectra clearly shows the effect of the Co doping, with the increase of the feature at the valence band maximum (VBM), i.e. near to 2 eV binding energy (attributed to the O 2p - Co 3d occupied states).

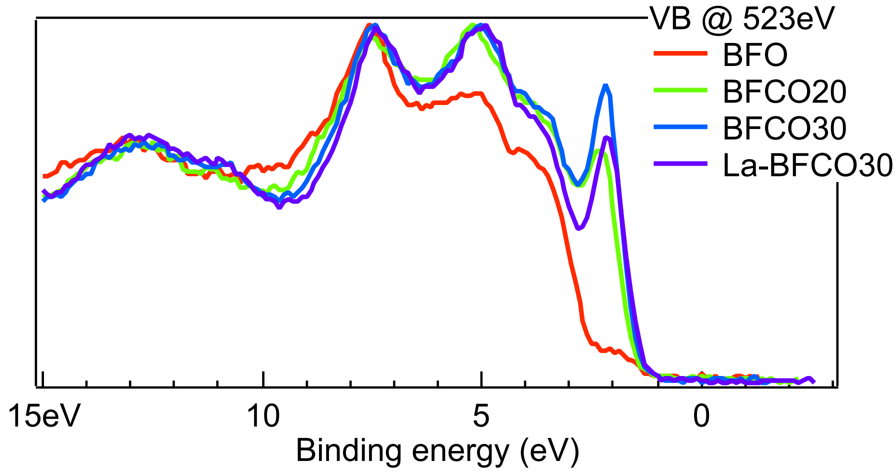


Fig. S3 Valence Band spectra of the BFO films with varying doping measured with a photon energy of 523 eV.

## 5 Piezoelectric characterization

In BFO, BFCO10 and BFCO30 LSMO-buffered 20 nm films piezoelectric characterization has been performed. Similar results to those show for the La-BFCO30 sample are obtained and these are summarized in Fig. S4.

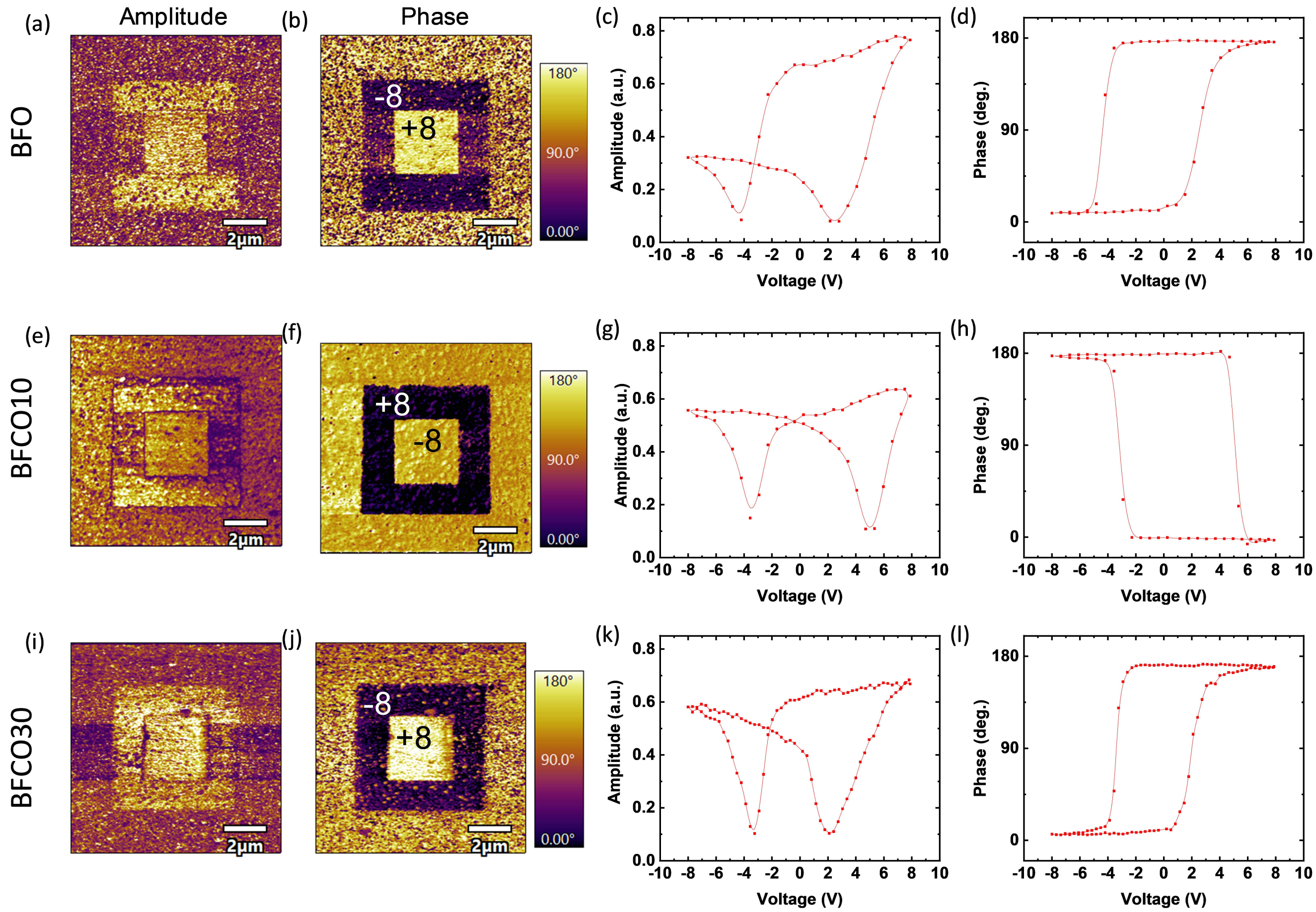


Fig. S4 (a,b) Amplitude and phase PFM images after electric lithography using -8 and +8 V in the regions indicated in the (c) image in a BFO LSMO-buffered 20 nm thick film. The outer region correspond to the as-grown state. (d,e) Amplitude and phase PFM loops in a BFO LSMO-buffered 20 nm thick film. (e,f,g,h) Equivalent to (a,b,c,d) for the BFCO10 sample. (i,j,k,l) Equivalent to (a,b,c,d) for the BFCO30 sample.

## References


1 R. D. Shannon, *Acta Crystallographica Section A*, 1976, **32**, 751–767.

2 J. Gebhardt and A. M. Rappe, *Physical Review B*, 2018, **98**, 125202.