Probing atom off-centering displacements in epitaxial strained $Sr_{1-x}Ba_xMnO_3$ thin films by HERFD-XANES

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$Sr_{1-x}Ba_xMnO_3$ (SBMO) perovskites are promising multiferroic materials due to the expected strong coupling between polar instability and spin order since both are driven by the Mn cation. Epitaxial SBMO films are then ideal candidates for tailoring the magnetoelectric properties since much larger tetragonal distortions can be imposed than in bulk samples by combining epitaxial strain with chemical doping (replacing Sr with Ba).

We have selected SBMO films with x=0.2 and 0.4 grown on (001)-oriented LSAT substrate. The thickness of the films was limited to 10 nm. A change in the tetragonality from $c/a<1$ (tensile strain 1.24% for x=0.2) to $c/a>1$ (compressive strain -0.36% for x=0.4) is induced with increasing the Ba content [1]. Strain-induced polar order was experimentally confirmed in epitaxial $SrMnO_3$ (SMO) films with 1.7% tensile strain [2] but it shows G-type antiferromagnetic (AF) order [3]. Despite the strains in SBMO films are still below the critical value (~3.5%) to induce ferromagnetism, a strong spin-phonon coupling has been demonstrated at the onset of the AF order in $Sr_{0.6}Ba_{0.4}MnO_3$/LSAT, which may lead to magnetoelectric coupling [4].

With the aim to probe the polar character of the SBMO/LSAT films, we performed Mn K-edge polarized HERFD-XANES measurements (in-plane and out-of-plane with ***E*** perpendicular and parallel to the *c* axis, respectively) acquired at the Mn Kα_1 emission line at ID26 beamline. The local off-centering of the Mn atom in its octahedral environment was investigated from the intensity variations in the pre-edge features, much better resolved in HERFD detection mode. The magnitude of the local displacements was quantified by comparison of the experimental linear dichroism spectra ($XANES_{out\text{-}of\text{-}plane}$ - $XANES_{in\text{-}plane}$) with theoretical FDMNES calculations [5]. We have determined a significant off-centering of the O atoms in the equatorial plane of the octahedron of about 0.05 Å along the in-plane <110> direction for tensile $Sr_{0.8}Ba_{0.2}MnO_3$/LSAT, similar to the behaviour found in polar SMO/LSAT [2] and $Sr_{0.7}Ba_{0.3}MnO_3$/TSO films [6] by scanning transmission electron microscopy (STEM). For compressive $Sr_{0.6}Ba_{0.4}MnO_3$/LSAT, out-of-plane polarization is expected but hard to be detected by STEM or second-harmonic generation (SHG) techniques. A significant off-centering of both Mn and equatorial O atoms of about 0.12 Å along the out-of-plane <001> direction is revealed by HERFD-XANES with Mn and O oppositely shifted along the *c* axis.

References

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