

unlikely, and there was no evidence (despite extensive study of samples with X-ray diffraction and transmission electron microscopy techniques) for such second phases. Furthermore, subsequent X-ray magnetic circular dichroism studies supported the assertion that this magnetism is not from a magnetic $\gamma\text{-Fe}_2\text{O}_3$ impurity phase [34]. To date, contradicting reports – including those of enhanced magnetism in nanoparticles of BiFeO_3 [35] as well as the observation of samples exhibiting no such enhancement – have been presented. It is thus fair to say that this is an issue that remains unresolved in a rigorous sense.

Today, much progress has been made in understanding the structure, properties, and growth of thin films of BiFeO_3 . High-quality epitaxial BiFeO_3 films have been grown via molecular beam epitaxy (MBE) [36,37], pulsed laser deposition [28,38], radio-frequency (RF) sputtering [39,40], metalorganic chemical vapor deposition (MOCVD) [41,42], and chemical solution deposition (CSD) [43] on a wide range of substrates including traditional perovskite oxide substrates (with lattice parameters ranging from 3.86 to 4.01 Å, covering a range from 2.5% compressive strain to 1.3% tensile strain) as well as Si [38,44] and GaN [45]. This work has shown that high-quality films, like those shown in Fig. 3, can be routinely produced. Typical X-ray diffraction θ – 2θ measurements (Fig. 3a) illustrate the state-of-the-art in terms of high-quality, fully epitaxial, single-phase films (data here are for a $\text{BiFeO}_3/\text{SrRuO}_3/\text{SrTiO}_3$ (001) heterostructure). Detailed X-ray diffraction analysis has shown that films possess a monoclinic distortion of the bulk rhombohedral structure over a wide range of thicknesses, but the true structure of very thin films (<15 nm) remains unclear [46]. The quality of such heterostructures can be probed further by transmission electron microscopy (TEM) (Fig. 3b) [47]. TEM imaging reveals films that are uniform over large areas and with the use of high-resolution TEM we can examine the atomically abrupt, smooth, and coherent interface between BiFeO_3 and a commonly used bottom electrode material SrRuO_3 . Detailed studies of such epitaxial oxide interfaces reveal

that the rules of semiconductor heteroepitaxy with regard to relaxation of misfit strain through the formation of interface dislocations are valid for oxides as well. In this specific example, the lattice mismatch between SrRuO_3 and BiFeO_3 is $\sim 0.3\%$ and thus pseudomorphic growth is possible for thicknesses of ~ 30 nm. Prior work has shown, for example, that the density of misfit dislocations does indeed scale with the lattice mismatch between the two layers [48].

3.2. Evolution of antiferromagnetism in BiFeO_3 thin films

As was discussed previously, the structure of BiFeO_3 can be characterized by two distorted perovskite blocks connected along their body diagonal or the pseudocubic $\langle 111 \rangle$ to build a rhombohedral unit cell. BiFeO_3 is also a G-type antiferromagnet with the moments confined to a plane perpendicular to the $\langle 111 \rangle$ -polarization directions and possesses symmetry that permits a small canting of the moments in the structure, resulting in a weak ferromagnetic moment of the Dzyaloshinskii–Moriya type [26,27]. Ederer and Spaldin suggested that only one easy magnetization axis in the energetically degenerate 111 -plane might be selected when the crystal is strained [31]. The application of the appropriate strain (not defined in this initial work) would likely break the degeneracy between the eight available orientation variants possible in this system, thereby lowering the energy of a single direction in the plane. Thus, one critical question concerning magnetism in multiferroics such as BiFeO_3 that is of both fundamental and technological importance is how this order parameter develops with strain and size effects. Using angle- and temperature-dependent X-ray linear dichroism measurements and photoemission spectromicroscopy, Holcomb et al. [49] discovered that the antiferromagnetic order in BiFeO_3 does evolve and changes systematically as a function of thickness and strain. Lattice mismatch induced strain is found to break the easy-plane magnetic symmetry of the bulk and leads to an easy axis of magnetization which can be

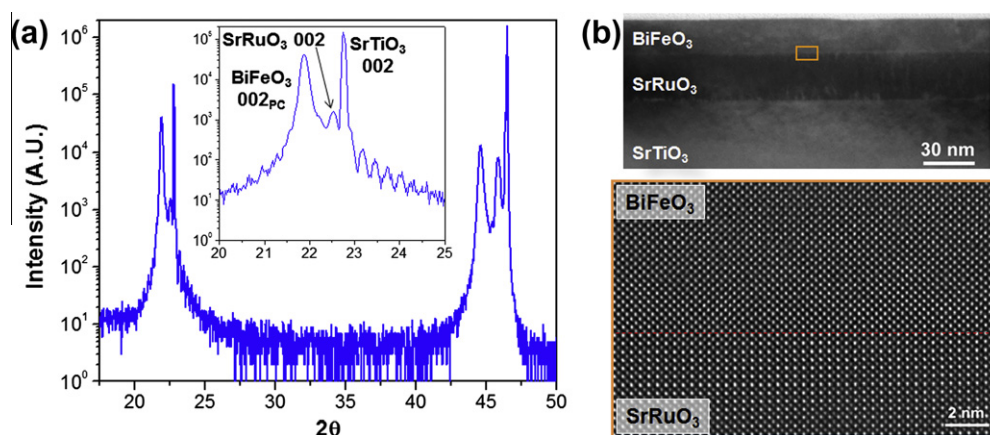


Fig. 3. (a) X-ray diffraction results from a fully epitaxial, single-phase $\text{BiFeO}_3/\text{SrRuO}_3/\text{SrTiO}_3$ (001) heterostructure (courtesy of A.R. Damodaran and L.W. Martin). (b) Low-resolution (top) and high-resolution (bottom) transmission electron microscopy images of $\text{BiFeO}_3/\text{SrRuO}_3/\text{SrTiO}_3$ (001) heterostructure (adapted from Ref. [47]).