($BaTiO_3$ [80], $PbTiO_3$ [81], $Pb(Zr_x,Ti_{1-x})O_3$ [82,83], and $BiFeO_3$ [84,85]) and spinel ($CoFe_2O_4$ [82,83], $NiFe_2O_4$ [81,84], and γ-Fe_2O_3 [85]) or corundum (α-Fe_2O_3 [85]) structures have been investigated. Pulsed laser deposition has proven to be a successful growth technique for achieving satisfactory properties in these nanostructured films [80,86,87].

The magnetoelectric coupling coefficients of such materials are often difficult to measure directly, because of issues arising from leakage in the materials. In many cases, the low resistance of the magnetic pillars penetrating through the films or the magnetic matrix limits the ability to probe these properties directly and could limit the efficacy of these vertical nanostructures in devices [88].

Zavaliche et al. [89] showed $\Delta E/\Delta H = 100$ V cm^{-1} Oe^{-1} at room temperature in a system comprising $CoFe_2O_4$ pillars embedded in a $BiFeO_3$ matrix. These films were analyzed with scanning probe techniques that utilized both magnetized and conducting tips. Typical surface morphology for such samples is shown in Fig. 7c. Magnetic measurements show the preference of such structures to maintain magnetization along the length of the nanopillars. Magnetic force microscopy scans both before (Fig. 7d) and after electric field poling (Fig. 7e) show that a significant number of $CoFe_2O_4$ pillars switch their magnetic state from a downward direction to an upward direction upon application of an electric field [90]. This work further showed that the magnetization-switching event was non-deterministic and could be improved by applying a small magnetic field (700 Oe) to the sample. This field is essential to break time reversal symmetry and overcome the degeneracy between the up and down magnetization states. Nonetheless, these structures have been shown to be very versatile and offer an excellent opportunity for electrically controlled magnetic storage.

3.7. Phase stability and self-assembled mixed phase nanostructures

Epitaxy presents a powerful pathway to control the phase stability and electronic properties in thin film systems, as has been well demonstrated in semiconductor heteroepitaxy [91]. The $BiFeO_3$ system presents a fascinating parallel in terms of how the phase stability in the system evolves with strain (or stress) imposed through heteroepitaxy. Although the structure of $BiFeO_3$ had been studied for many years [21,22,18], in 2005 the structural stability of the parent phase had come into question [92,93]. This was followed, in turn, by a number of thin film studies reporting that a tetragonally distorted phase (derived from a structure with $P4mm$ symmetry, $a \sim 3.665$ Å, and $c \sim 4.655$ Å) with a large spontaneous polarization may be possible [92,94,95]. But it was the report of the so-called mixed-phase thin-films possessing tetragonal- and rhombohedral-like phases in complex stripe-like structures that give rise to enhanced electromechanical responses [96] that really launched this field. Zeches et al. observed that the rhombohedral bulk crystal structure of the parent phase

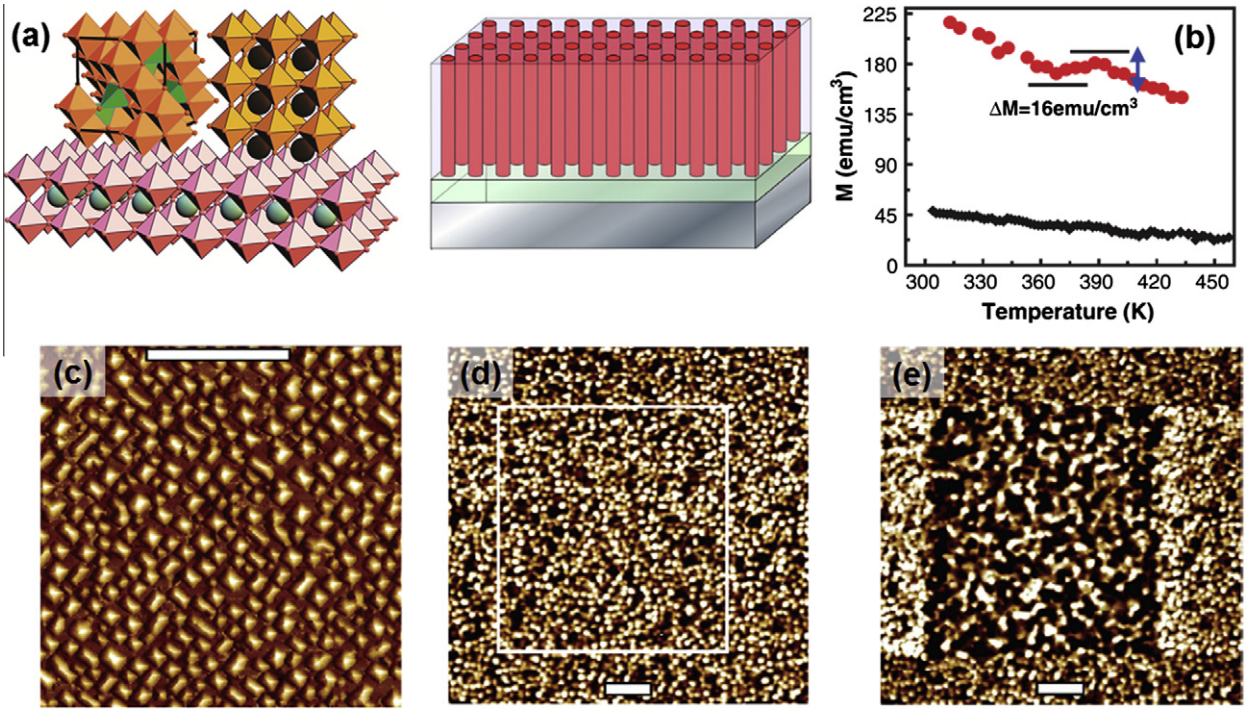

Fig. 7. Multiferroic nanostructures. (a) Schematic illustrations of vertical nanostructure of spinel pillars embedded in a perovskite matrix grown on a perovskite substrate. (b) Magnetization vs. temperature curve measured at 100 Oe, showing a distinct drop in magnetization at the ferroelectric Curie temperature – proof of strong magnetoelectric coupling. (c) Surface topography of a $CoFe_2O_4/BiFeO_3$ nanostructure as imaged by atomic force microscopy. Magnetic force microscopy scans taken in the same area before (d) and after electrical poling at −16 V (e) (scale bars are 1 μm) (adapted from Refs. [79,90]).