Room temperature multiferroic oxide films

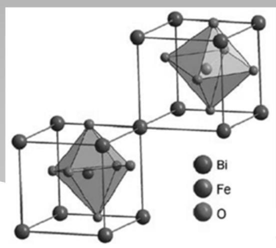
- Multiferroic is used to describe materials that possess two or all three of the ferro-properties: ferroelectricity, ferro/ferrimagnetism, and ferroelasticity.
- large magneto-electric coupling where the manipulation of magnetization or polarization can be achieved by applying an electric or magnetic field, respectively.
- rarity of ferromagnetic ferroelectricity was due to the contra-indication between magnetism and ferroelectricity (empty d orbital vs. partially filled d orbital)

Materials

- The only example of a single-phase material showing both electric and magnetic orderings well above room temperature is $BiFeO_3$, which is ferroelectric and antiferromagnetic.
- combine a ferro-electric phase and a ferromagnetic phase into a composite

BiFeO3

- distorted perovskite structure (R3C) with a= 3.96A and α= 89.4°
- Fe ions are displaced from the center along the [111] direction
- Ferroelectricity, Tc= 830°C
  - ➔ [111] direction with the largest polarizability
- G-type Antiferromagnetism, T_N= 370°C
  - ➔ spins in BiFeO3have a spiral structure but the total moment is cancelled out.
  - ➔ bulk BiFeO3does not show any ferromagnetism



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Ferroelectric domains

The ferroelectric polarization in BiFeO3 is along the f [111] directions that have eight possible orientations.

➔ The direction of the polarization can be switched by three different angles, namely 180°, 109° and 71°.

➔ only switching of the polarization by either 109° or 71° could cause the reorientation of antiferromagnetic plane. (2006 Ramesh)

➔ ferroelectric domain structures by piezo force microscopy

➔ antiferromagnetic orientation by X-ray photoemission electron microscopy

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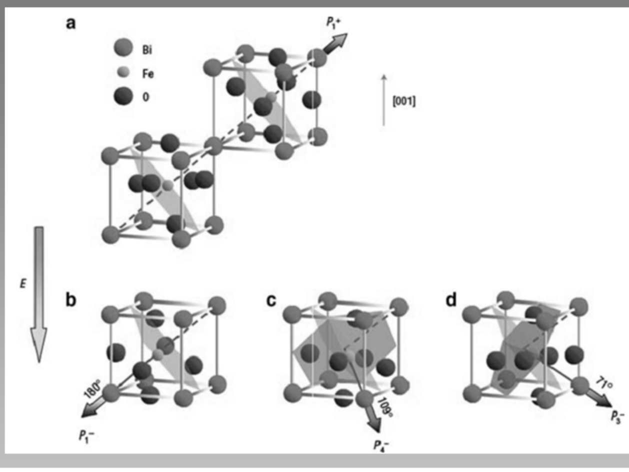

Fig. 3.23 Schematics of the reorientation of antiferromagnetism (*shaded planes*) by switching the polarization (*arrows*): (**a**) Before applying an external electric field, the polarization is along [111] direction pointing up; (**b**) After applying an external field, the polarization was switched 109° with the out-of-plane component switched down. However, the antiferromagnetic plane remains unchanged; when the polarization is switched 109° (**c**) and 71° (**d**), the antiferromagnetic plane reoriented from the original plane to the new green and blue planes, respectively (Reproduced from [91])

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Research reports

First principle calculation:

➔ the spontaneous polarization along the [111] direction resulted in a value 95 μC/cm^2

2005, Ramesh, epitaxial BiFeO3 grown on SrTiO3 substrates

➔ 50 –60 μC/cm^2, ten times larger than the BFO single crystal, due to strain effect

➔ ferromagnetism!!

Ederer et al. suggeste: (X)

➔ a local canting of the antiferromagnetic sublattice occurs in thin films

➔ very weak ferromagnetism of 0.1 μB/unit cell << reported saturation moments (as high as 1μB/Fe) by the exp. of Wang

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2005, Eerenstein et al.:

- The enhancement of magnetism was not due to the strain effect but rather from Fe2+ ions induced by the oxygen vacancies
- how the film thickness impacted the magnetic moments or the oxygen vacancies ??

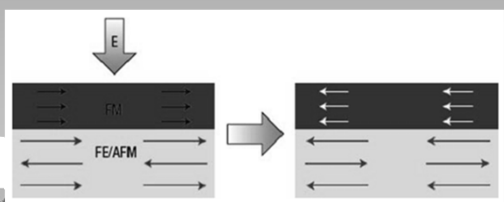
2006, Ramesh:

- switching the polarization reoriented the antiferromagnetic domains in BiFeO3 thin films

Voltage controlled exchange bias

Exchange bias, also known as Exchange anisotropy occurs at an interface between an antiferromagnet and a ferromagnet.

- hysteresis loop of the ferrimagnet will be shifted
- widely used in magnetic recording and sensing
- electric tuning of exchange bias could be used in the BFO system



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CoFe/Cu/CoFe/BiFeO3 spin valve

2007, Martin et al.

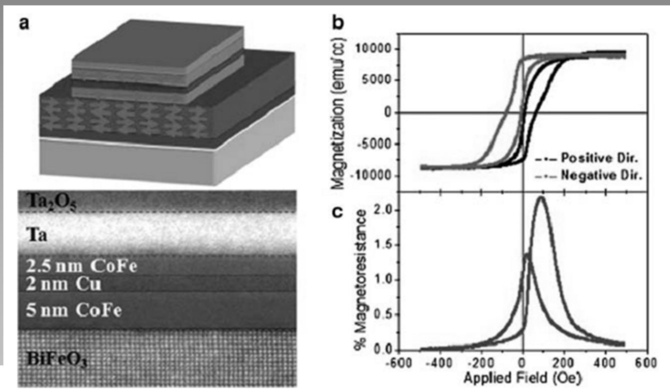
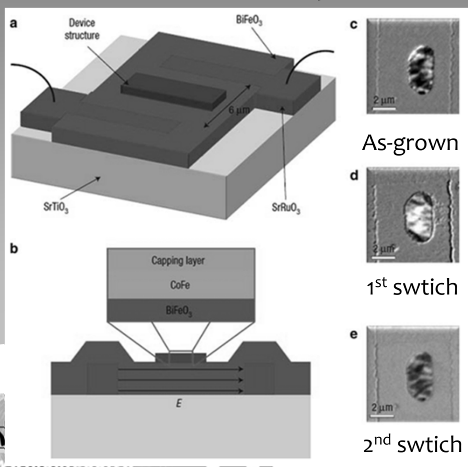


Fig. 3.25 CoFe/Cu/CoFe/$BiFeO_3$ spin valve (**a**) Schematic of the spin valve structure (*top*) and spin valve structure (*bottom*) illustrated on a Scanning Transimission Electron Microscopy image of the multilayers; (**b**) Hysteresis loops of the spin valve; (**c**) Magnetoresistance of the spin valve

electrically controlled exchange bias using CoFe/BiFeO3

2008, Ramesh

The electric field across BiFeO 3 rotated the magnetization by 90°



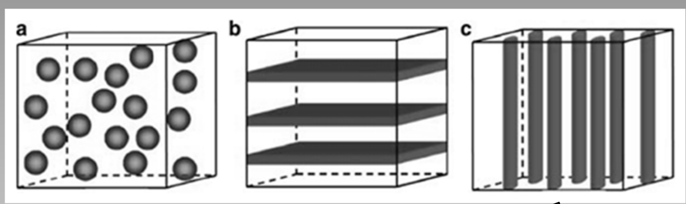
X-ray Magnetic Circular Dichroism–Photoemission Electron Microscopy

Multiferroic Composites

- multiferroicity only occur at very low temperatures for the single phase materials
- artificial composites by combining piezoelectric (ferroelectric) and ferromagnetic materials have gained popularity
- Namely artificial multiferroics or metamultiferroics
- the magnetoelectric effect comes from the product of the magnetorestrictive effect in the magnetic phase and the piezoelectric effect in the piezoelectric phase
- larger magnetorestrictive coefficients and large piezoelectric coefficients are preferred

Types

Particulate structure
multilayer/superlattice structure
columnar structure



storage technology

Self-assembled nanocolumnar structure

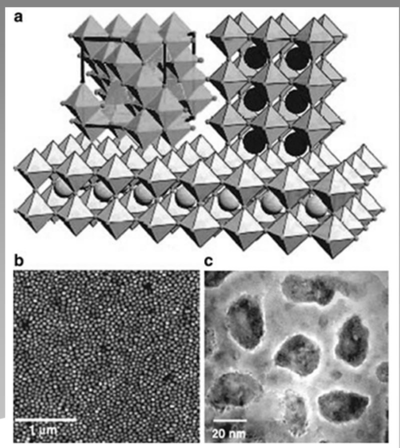


Fig. 3.28 (**a**) Epitaxial structure of a spinel/$CoFe_2O_4$ (*top left*) and a perovskite/$BaTiO_3$ atop perovskite substrate (*top right*); (**b**) Atomic force microscopy image shows the arrangement of $CoFe_2O_4$ nano-pillars; (**c**) Transmission electron microscopy plan-view image of the $CoFe_2O_4/BaTiO_3$ microstructure. The dark contrast region in the image represents the $CoFe_2O_4$ pillars (Reproduced from [99])

2004, 2005, Ramesh
- ◆ CoFe2O4 nanopillars have uniform size and average spacing of 20–30 nm

2007, Zavaliche
- ◆ 180º rotation of the magnetization of CoFe2O4 pillars by applyinga very weak external magnetic field with the assistance of an electric field.
- ◆ Namely, electrically assisted magnetic writing

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