Multiferroics for spintronics

Manuel Bibes[2]

H. Béa[1], M. Gajek[1], X.-H. Zhu[1], S. Fusil[1], G. Herranz[1], M. Basletic[1], B. Warot-Fonrose[3], S. Petit[4], P. Bencok[6], K. Bouzehouane[1], C. Deranlot[1], E. Jacquet[1], A. Barthélémy[1], J. Fontcuberta[5] and A. Fert[1]

[1] Unité Mixte de Physique CNRS / Thales, Orsay (FRANCE)

[2] Institut d'Electronique Fondamentale, CNRS, Université Paris-Sud, Orsay (FRANCE)

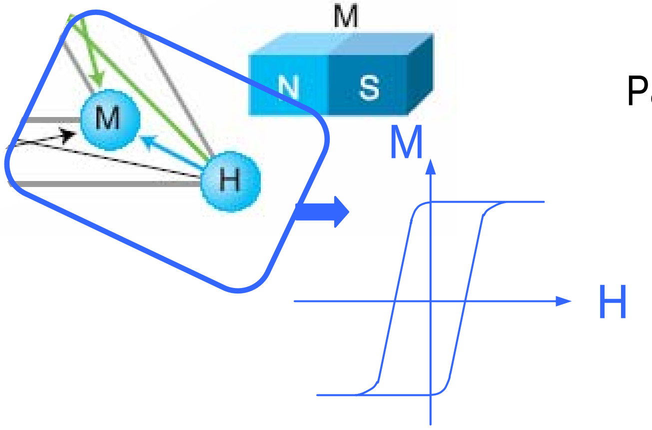
[3] CEMES, CNRS, Toulouse (FRANCE)

[4] Laboratoire Léon Brillouin, CEA, Saclay (FRANCE)

[5] ICMAB, CSIC, Campus de la UAB, Bellaterra (SPAIN)

[6] European Synchrotron Radiation Facility, Grenoble (FRANCE)

Ferromagnetic materials



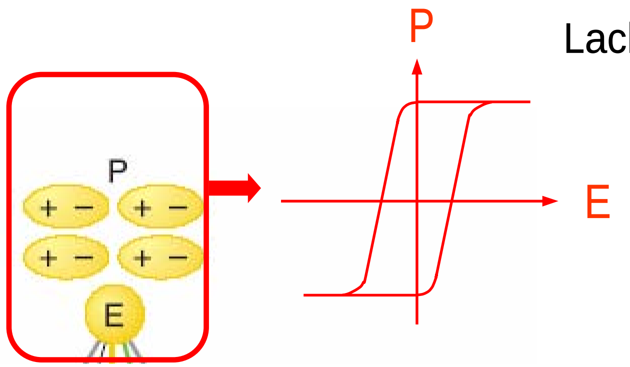
Partially filled d/f shells

Magnetic Data Storage

Spintronics

Switchable parameter : M
External stimulus : H

Ferroelectric materials



Lack of inversion symmetry

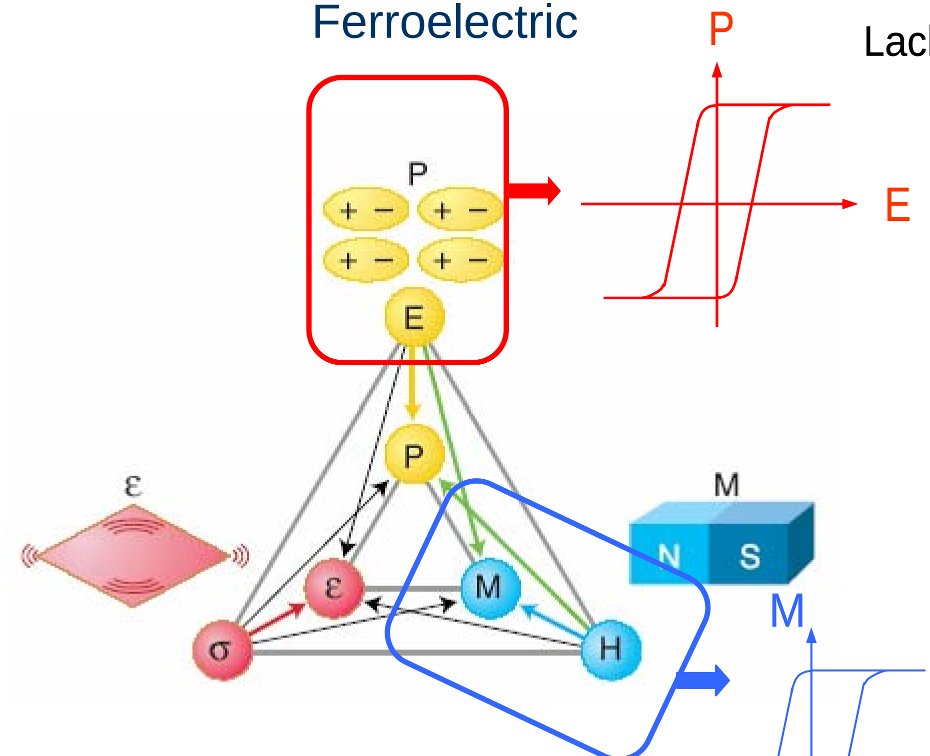
Sensors

FeRAM

Switchable parameter : P
External stimulus : E

Multiferroic materials

Ferroelectric

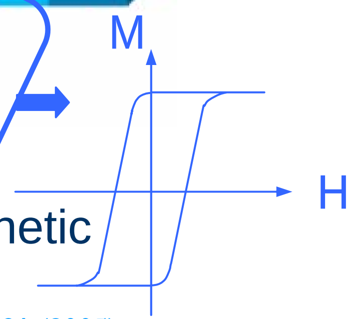


Lack of inversion symmetry

Sensors

FeRAM

Partially filled d/f shells



Magnetic Data Storage

Spintronics

Ferroelastic

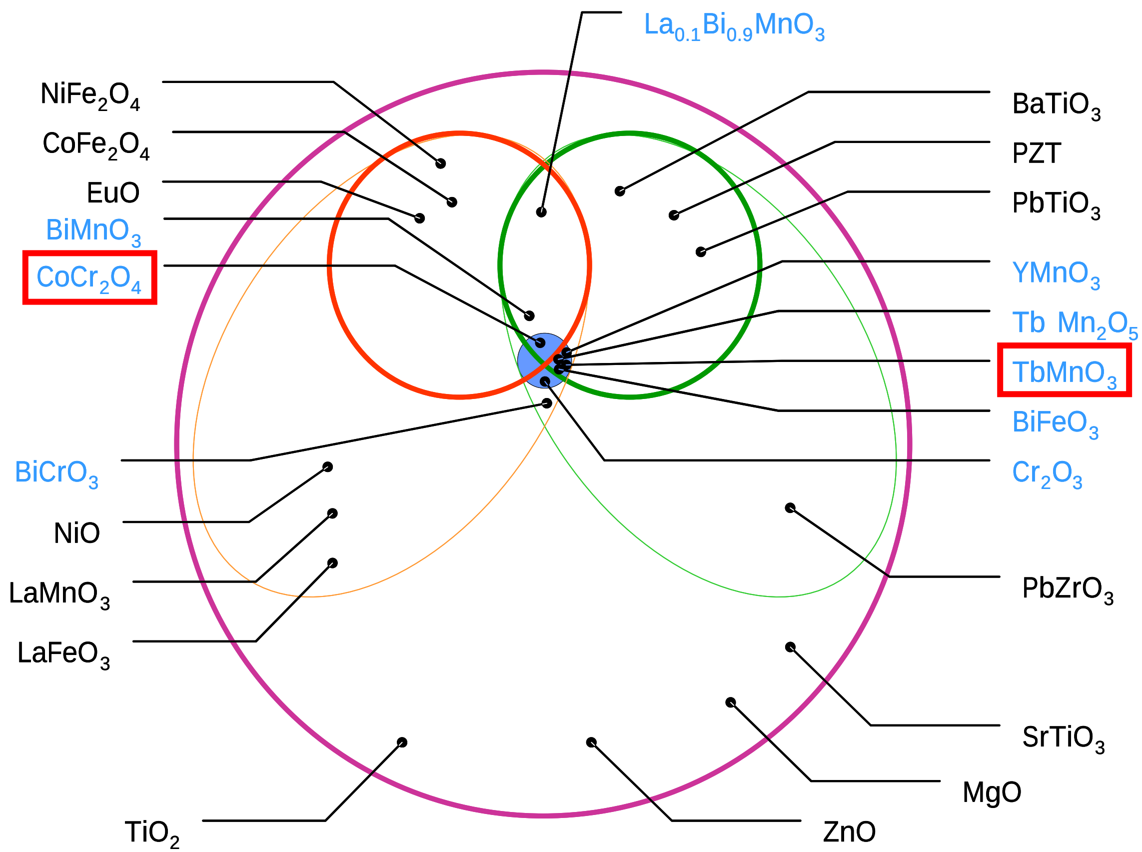
Ferromagnetic

From Spaldin and Fiebig, Science 309, 391 (2005)

Switchable parameter : M, P
External stimulus : H, E

- **Multiple-state memories**
- M switching by E
- P switching by H

Insulating oxides : a classification



Magnetically polarizable
Ferro(i)magnetic

Electrically polarizable
Ferro(i)electric

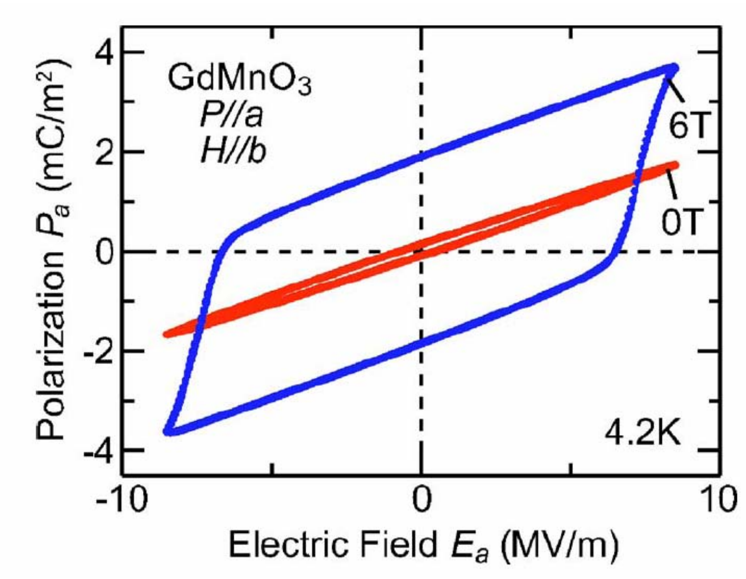
Magnetoelectric

Derived from Eerenstein, Mathur and Scott, Nature 442, 759 (2006)

Multiferroics - examples of magnetoelectric coupling

$(Gd,Dy,Tb)MnO_3$: spiral magnets

Spiral ordering breaks inversion symmetry
➔ (improper) ferroelectricity appears
(but **no** finite magnetization)

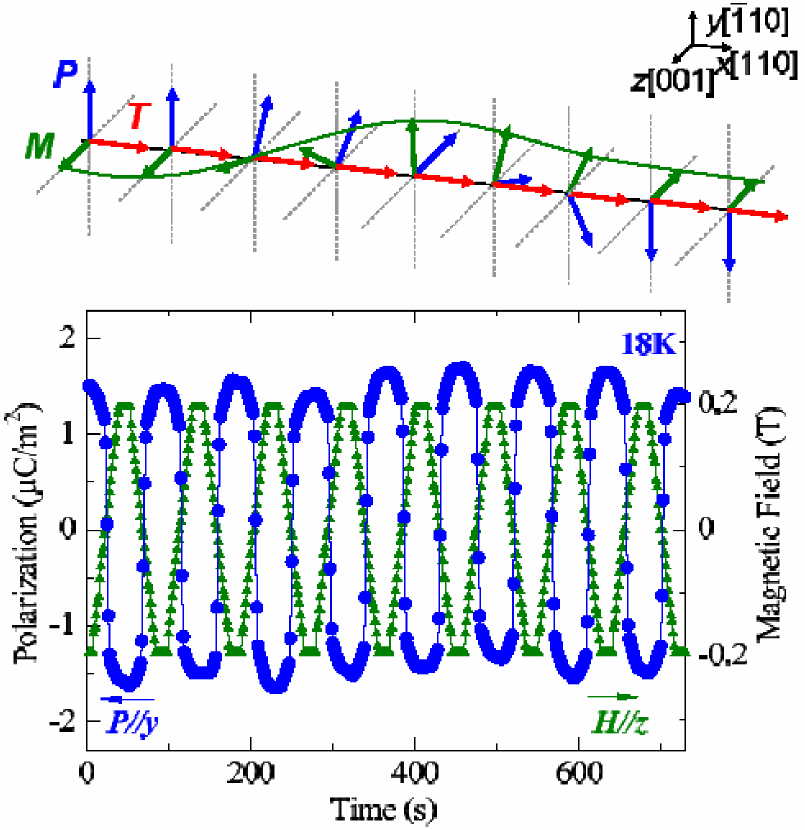


Apply a magnetic field : change magnetic state
➔ switch polarization on/off

Kimura et al, PRB 71, 224425 (2005)

$CoCr_2O_4$: conical magnet

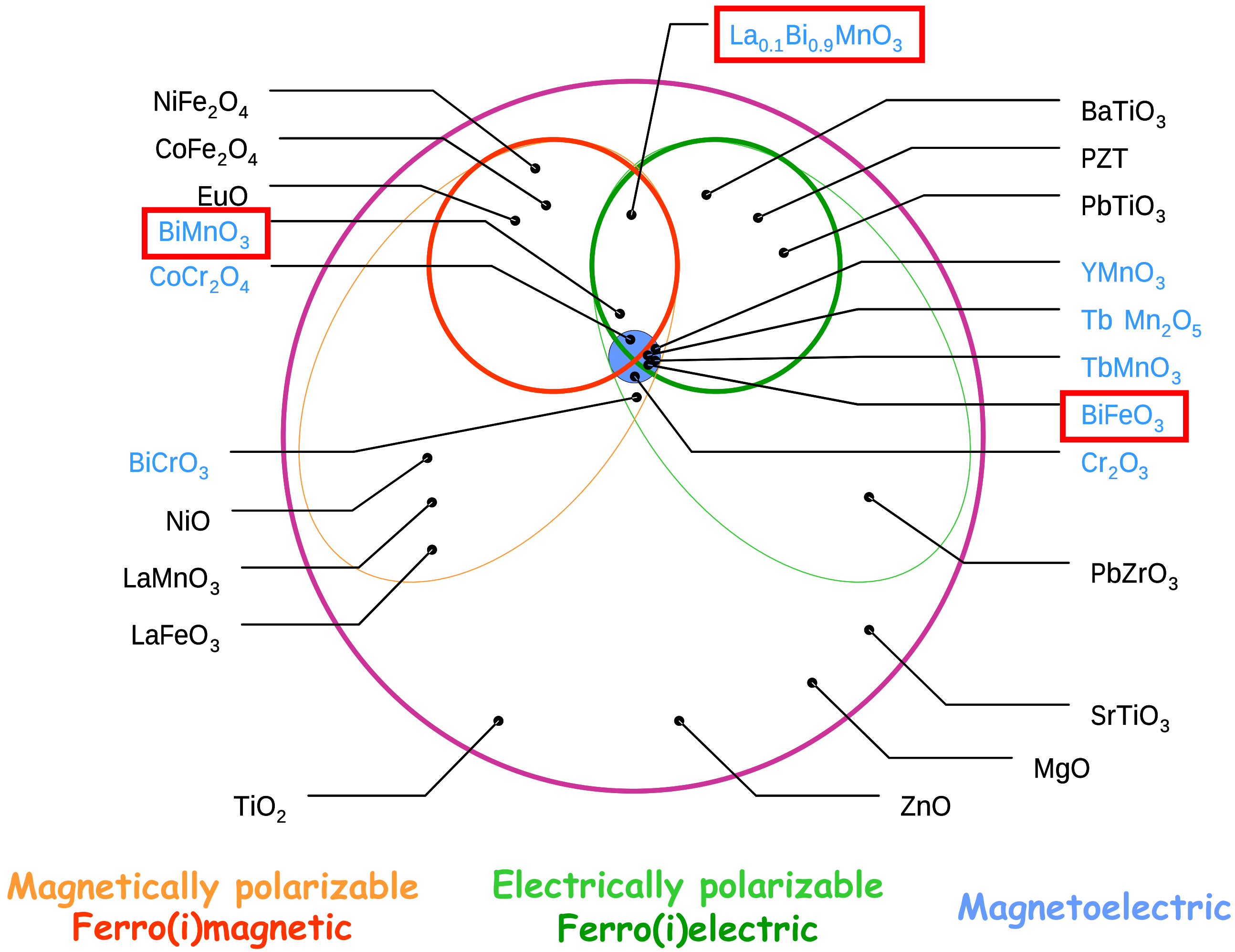
Conical ordering breaks inversion symmetry
➔ (improper) ferroelectricity appears
(**with** a finite magnetization)



Flip polarization direction by a magnetic field

Yamasaki et al, PRL 96, 207204 (2006)

Insulating oxides : a classification



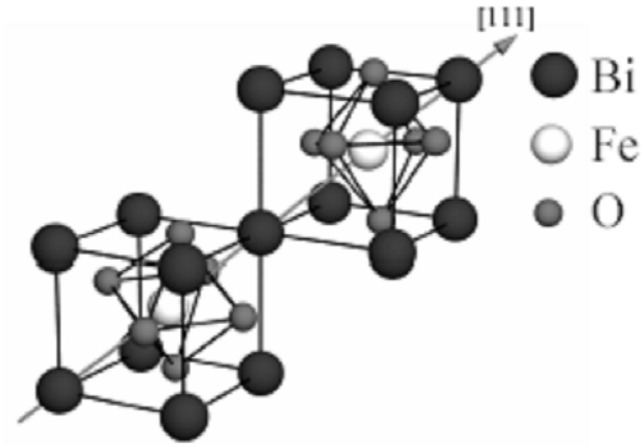
Derived from Eerenstein, Mathur and Scott, Nature 442, 759 (2006)

$BiFeO_3$

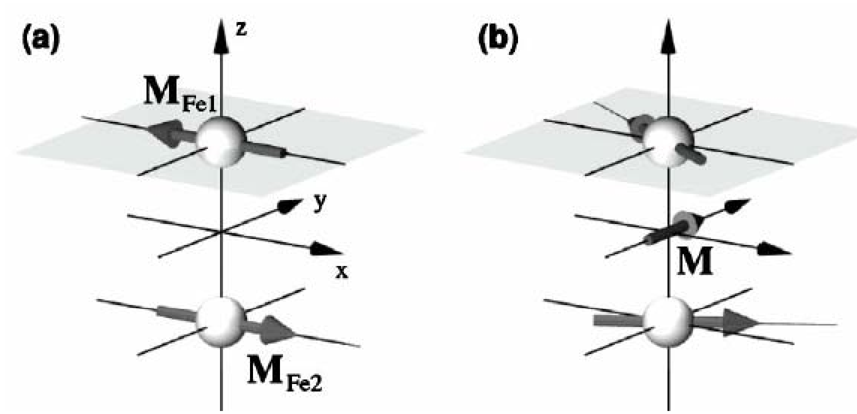
A room-temperature antiferromagnetic ferroelectric

$BiFeO_3$: bulk properties

Rhombohedral Perovskite (R3c)
a=3.96Å, α=89.4°



Neaton et al. Phys. Rev. B, 71, 014113 (2005)



Ederer et Spaldin, Phys. Rev. B, 71, 060401 (R) (2005)

Ferroelectric

T_C=1100K
P_S=6µC/cm² (1970 paper, bad crystal)
J. R. Teague et al., Solid State Commun., 8, 1073 (1970)

P_S=60µC/cm² (2007 paper, good crystal)
D. Lebeugle, M. Viret et al, PRB in press
Condmat/0706.0404

G-type Antiferromagnetic

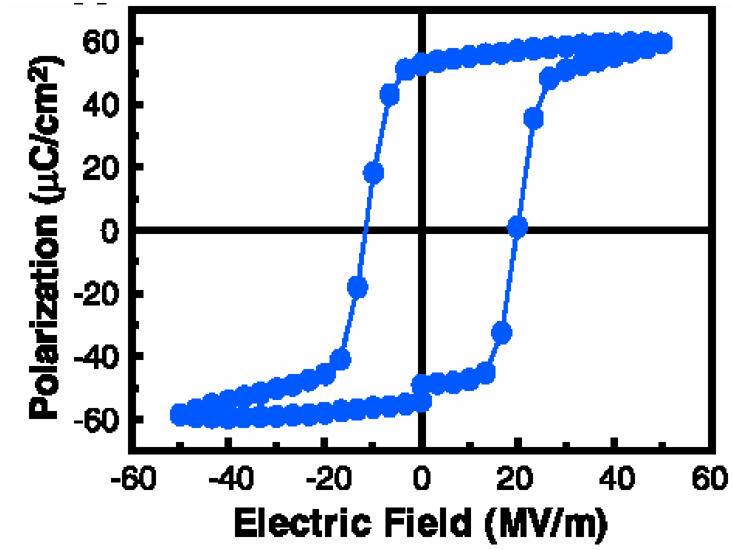
T_N=640K
Canted spins → weak FM
M_S=0.01μ_B/f.u.
Incommensurate cycloidal modulation

P. Fisher et al., J. Phys. C,13, 1931 (1980)
Popov et al. in Magnetoelectric Interaction Phenomena in Crystals (NATO Science Series, 2004) p. 277

$BiFeO_3$: thin films properties

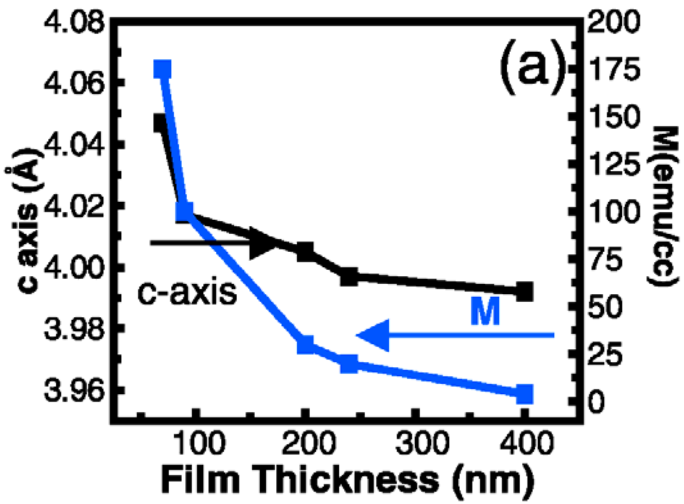
Wang et al., Science, 299, 1719 (2003) : BFO//STO (001)

t_{BFO}=200nm : P_S=55µC/cm²



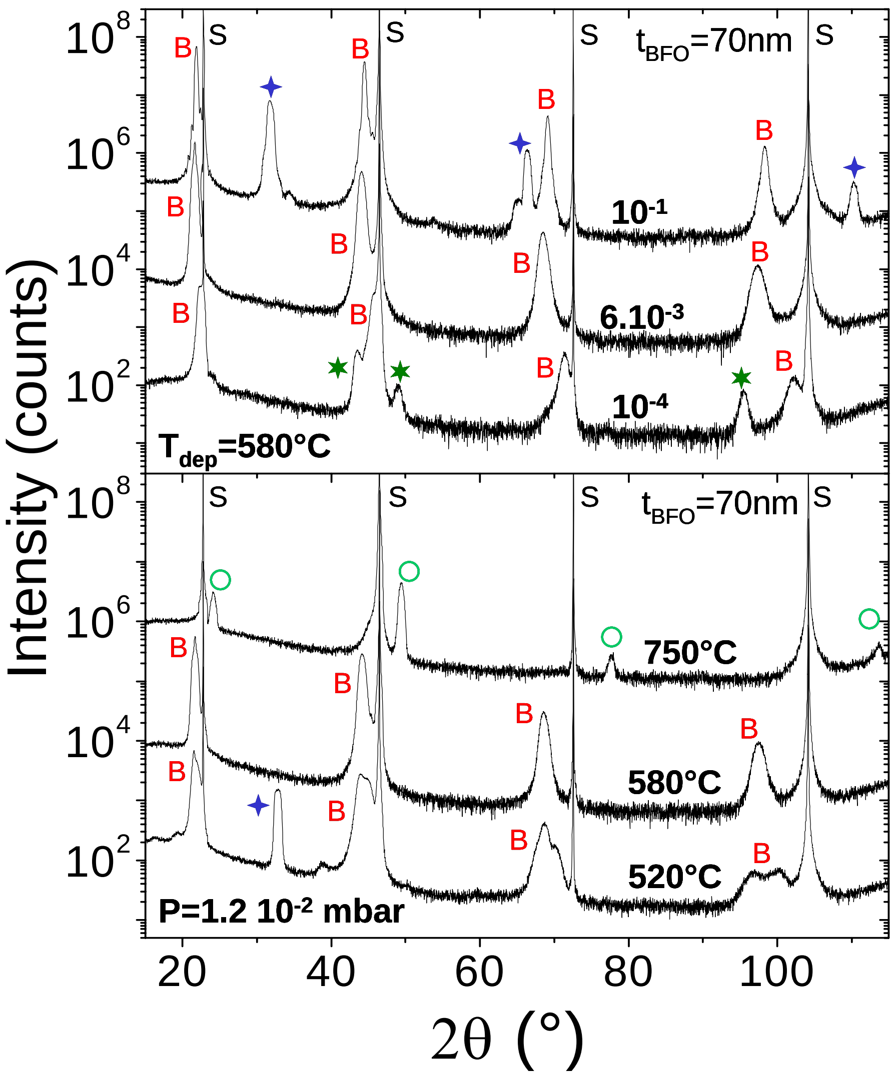
t_{BFO}=70nm : M_S=150emu/cm³ (~1μ_B/fu)

t_{BFO}=400nm : M_s=5emu/cm³ (0.03μ_B/f.u.)



Claim of enhanced polarization and magnetization compared to bulk

Growth of $BiFeO_3$ thin films



B: $BiFeO_3$, S: $SrTiO_3$,
*: γ-Fe_2O_3, O: α-Fe_2O_3, ✦:Bi_2O_3

Pulsed laser deposition on $SrTiO_3$ (001)
Target : $Bi_{1.15}FeO_3$

Growth conditions : T=580°C, $P_{O2}=6.10^{-3}$mbar

Bi much more volatile than Fe :

- low P or high T (Bi evaporates more than Fe)

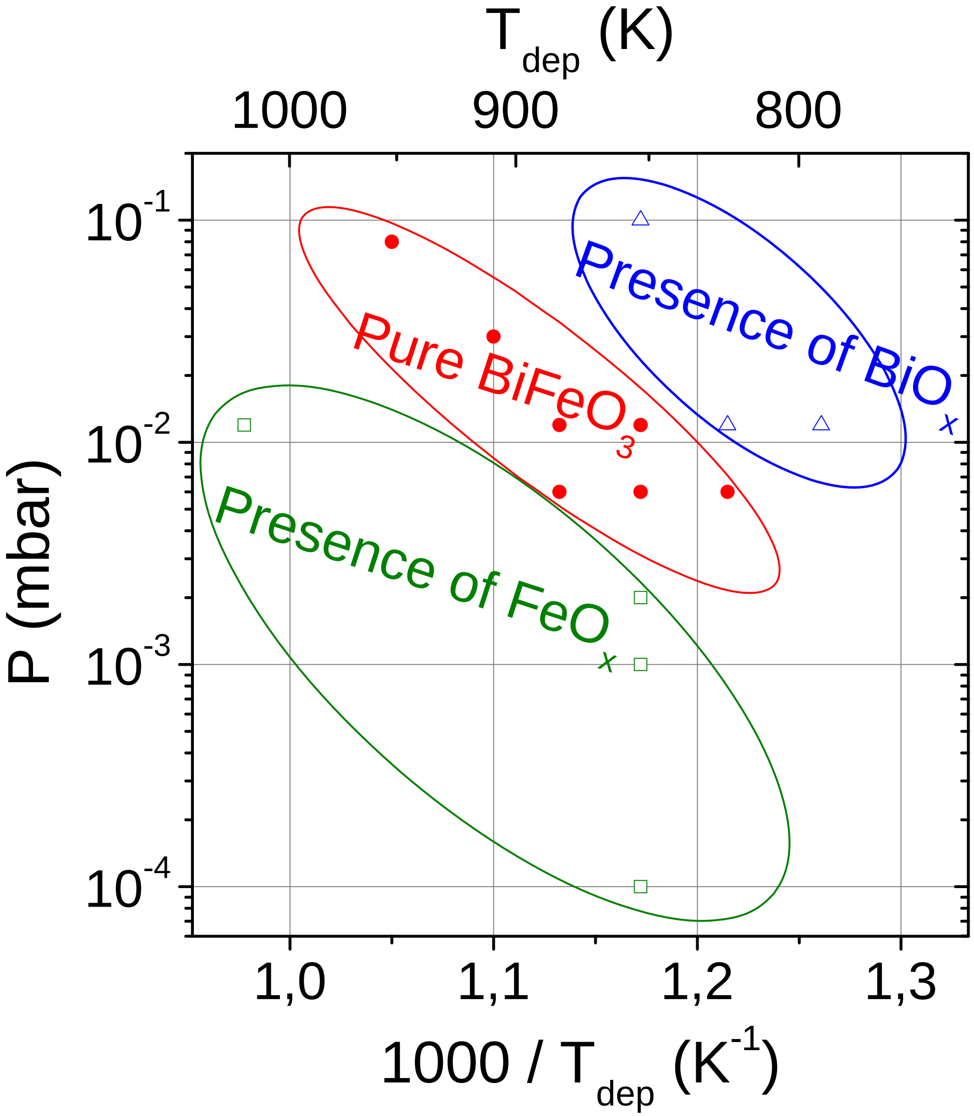
⇒ Fe oxides

- high P or low T (excess Bi)

⇒Bi oxides

Growth of $BiFeO_3$ thin films

Phase diagram

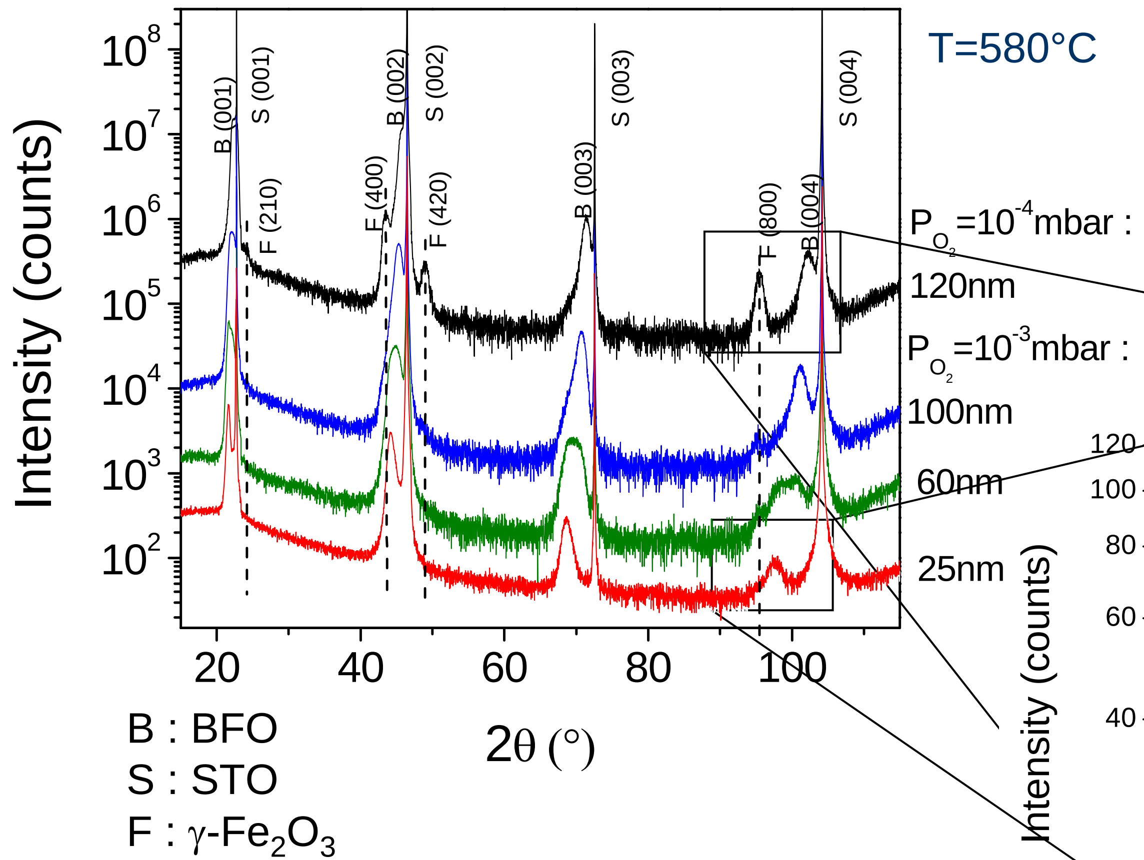


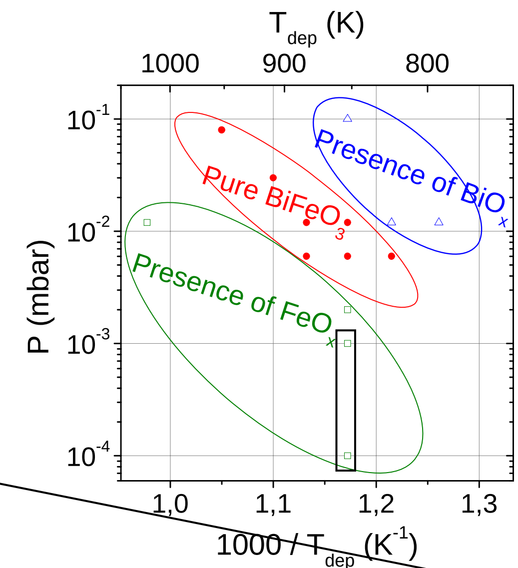
Pure $BiFeO_3$ obtained in a very ***narrow region*** around T_{dep}=580°C and P_{O2}=6.10^{-3}mbar

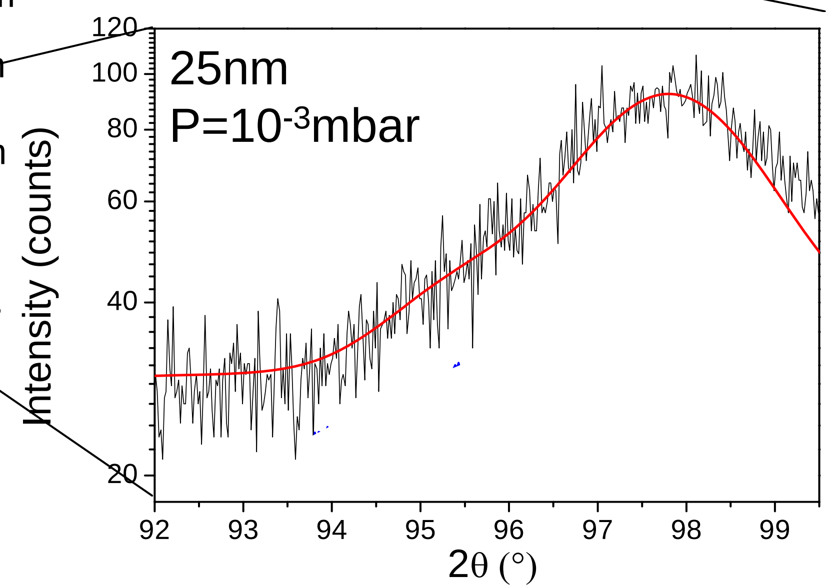
Appl. Phys. Lett.,87, 072508 (2005)

Growth of $BiFeO_3$ thin films – Parasitic Fe-rich phases

X-ray diffraction



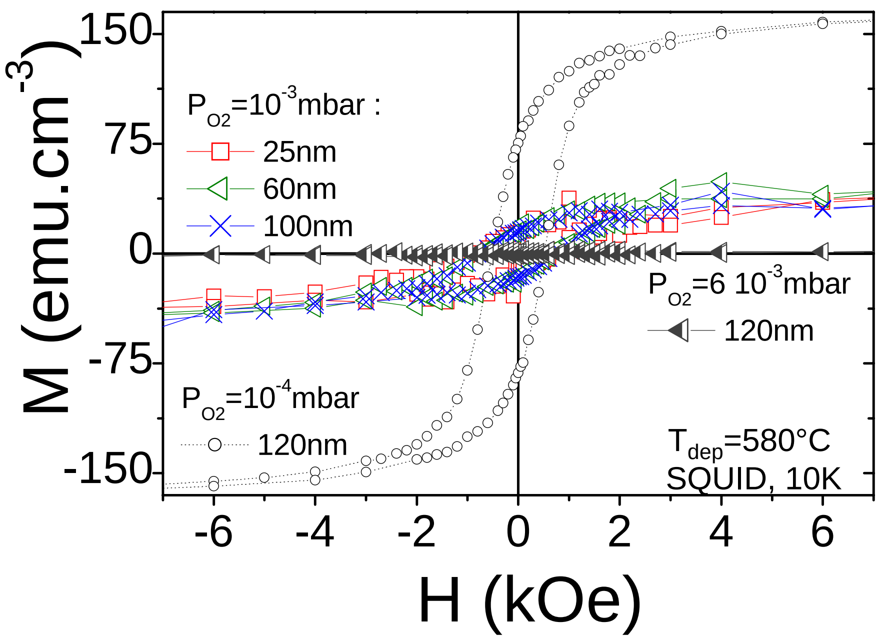


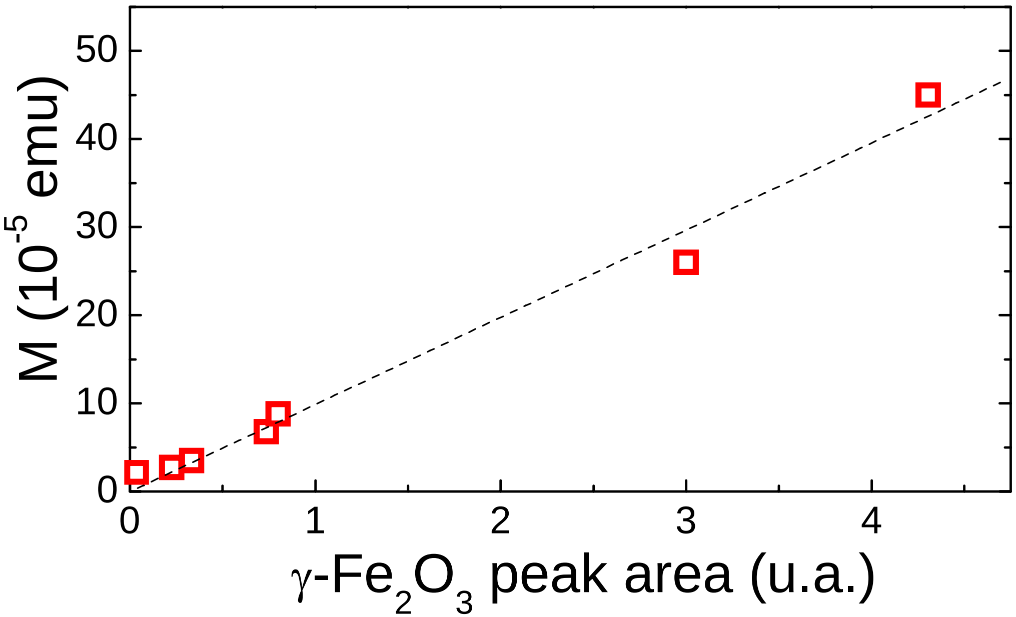


Quantification of γ-Fe_2O_3 by XRD : ***not easily detectable***

Growth of $BiFeO_3$ thin films – Parasitic Fe-rich phases

SQUID measurements





BFO + γ-Fe_2O_3 : up to M_s~150emu/cm³
γ-Fe_2O_3 ferrimagnetic (M_s=430emu/cm³)
Pure BFO : M_s~2emu/cm³

Magnetic moment comes from γ-Fe_2O_3

Phys. Rev. B, 74, 020101R (2006)

BFO weak bulk-like ferromagnetic moment

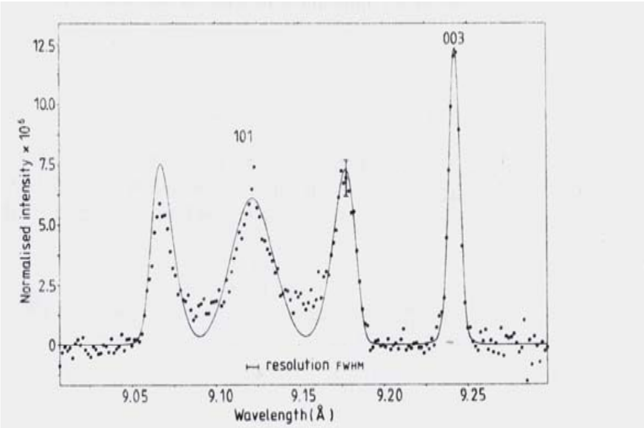
Similar conclusions :

Eerenstein et al. Science, 307 1203a (2005)

Wang et al., Science, 307, 1203b (2005)

(001) $BiFeO_3$ films – Magnetic properties

Neutron diffraction

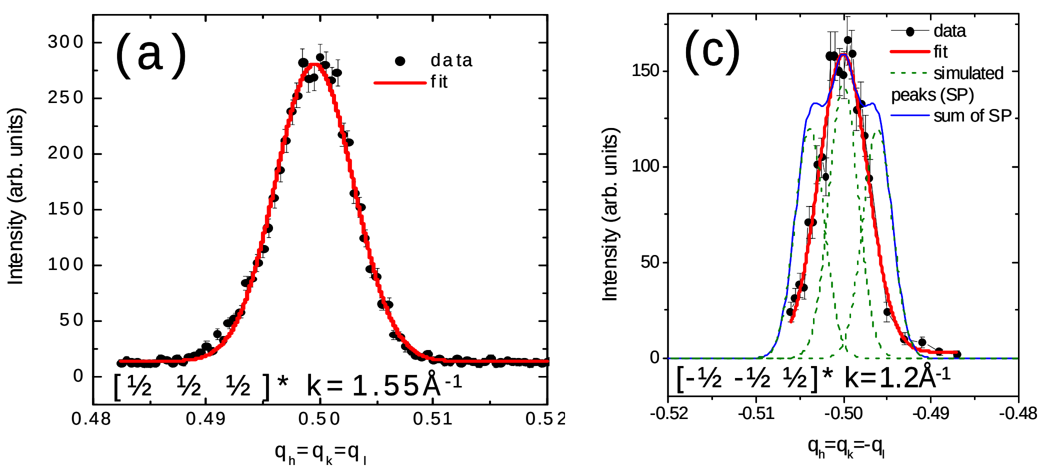


from Sosnowska et al., J. Phys. C, 15, 4835 (1982)

In R3c bulk BFO :
$[003]^*_H$ single peak → ***G-type*** antiferromagnet
$[101]^*_H$ peak with satellites → ***cycloidal modulation***
⇒ ***Averaging to zero*** of the linear ME effect

In pseudo-cubic notation : $[003]^*_H \rightarrow [½\ ½\ ½]^*_C$
$[101]^*_H \rightarrow [-½\ -½\ ½]^*_C$

BFO(240nm)//STO (001)

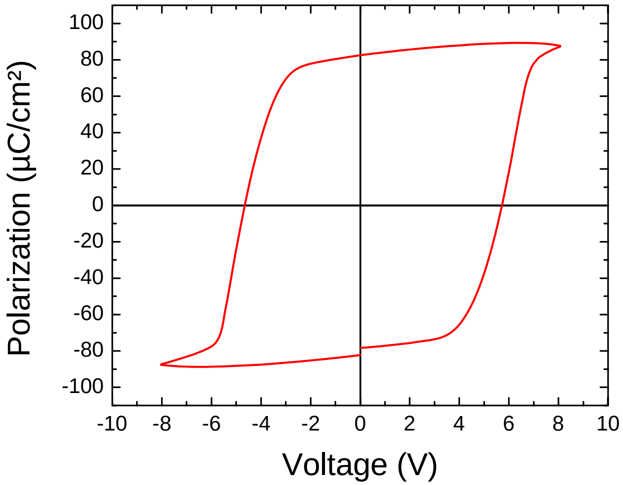


- ***G-type antiferromagnetic order*** as in bulk BFO
- ***No cycloidal modulation*** contrary to bulk BFO
- Linear magnetoelectric effect ***allowed***

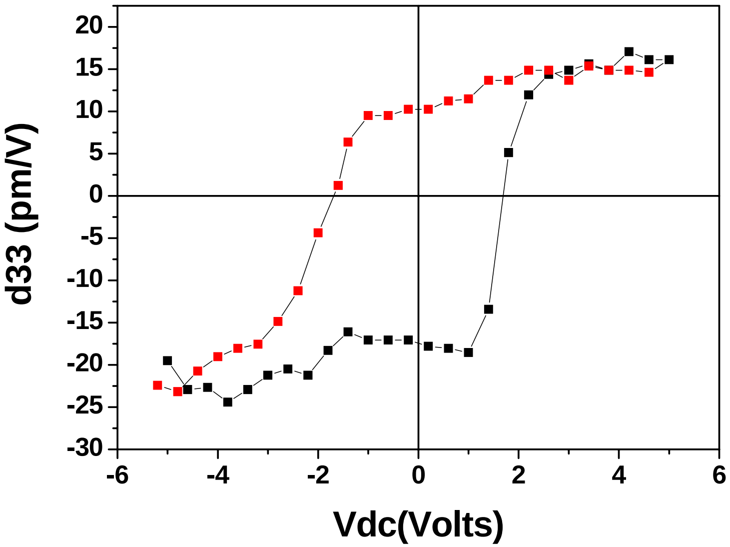
Phil. Mag. Lett. 87, 165 (2007)
(Special issue on multiferroic thin films Eds. N.D. Mathur and MB)

(001) $BiFeO_3$ films – Ferroelectric properties

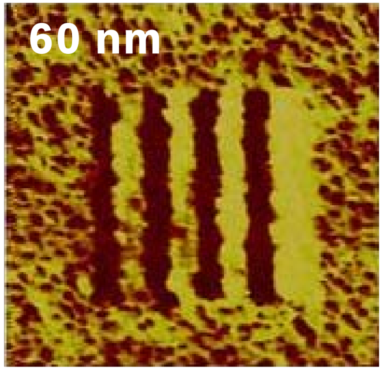
Polarization loops

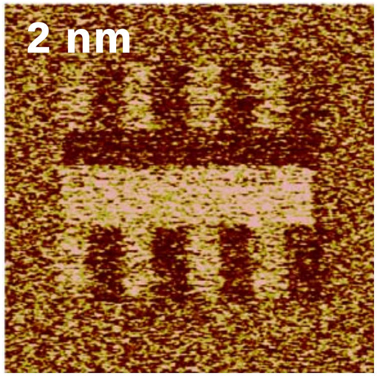


Piezoelectric loops



Piezoresponse force microscopy

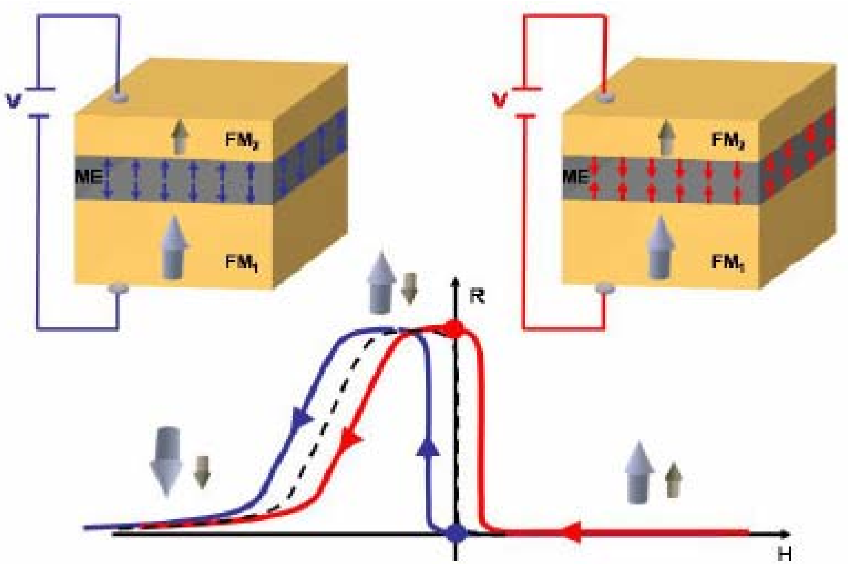




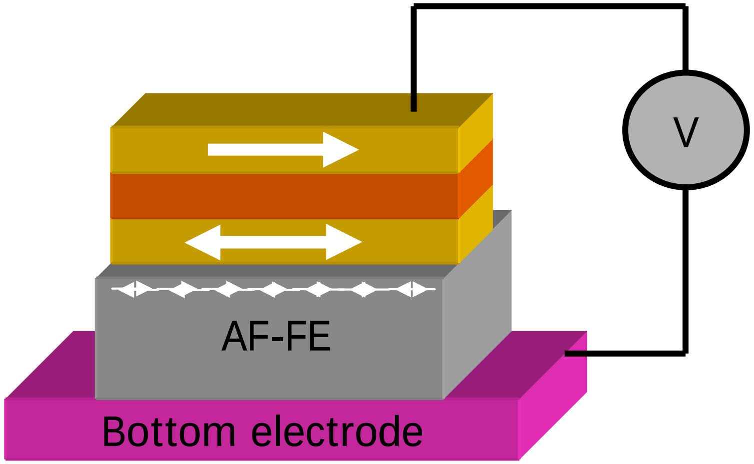
- BFO films are ferroelectric with a large polarization (~70 µC/cm²) and piezoelectric with a d_{33} coefficient of ~20 pm/V
- Ferroelectricity is preserved down to 2 nm.

Jpn. J. of Appl. Phys., 45, L187 (2006)

Principle : voltage-controlled exchange bias



Binek et Doudin, JPCM, 17, L39 (2005)



Spin-valve on top of a ***multiferroic film*** (FE and AFM)

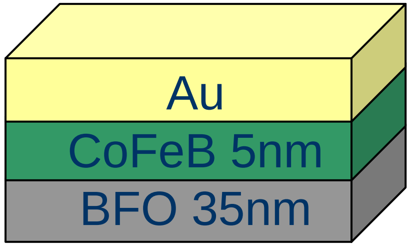
Magnetic tunnel junction with ***multiferroic barrier*** (FE and AFM)

Electric field control of the junction resistance state

Prerequisites :

1. observe robust exchange bias at room-temperature
2. spin-dependent tunneling through multiferroic barrier
3. switch exchange bias direction by E-field (magnetoelectric coupling)

Exchange bias with $BiFeO_3$ films

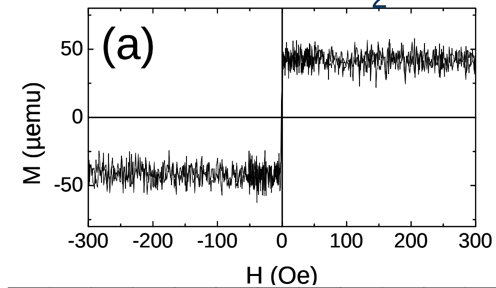


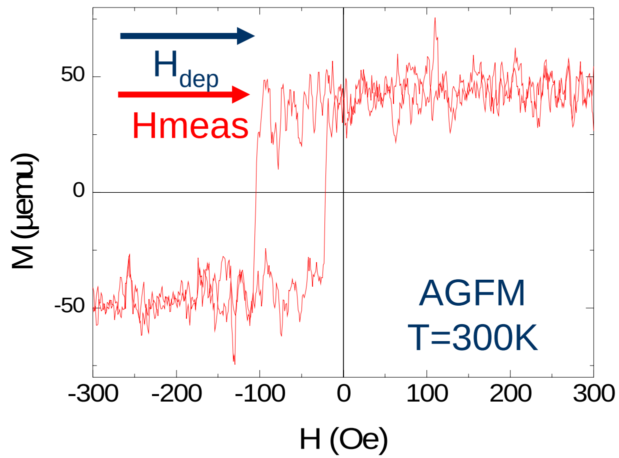
CoFeB deposited by sputtering

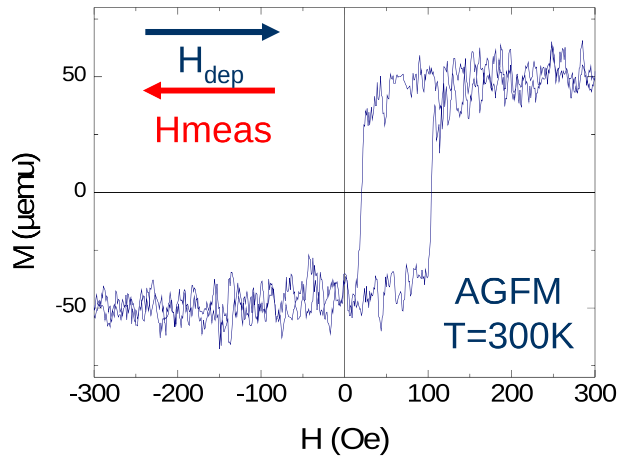
H_c=42Oe, ***H_e=-62Oe***

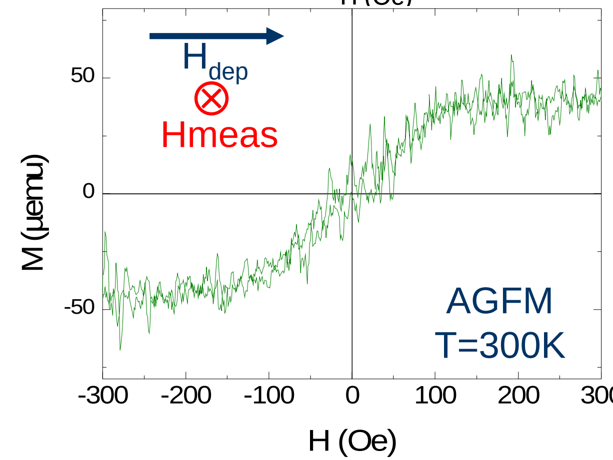
Appl. Phys. Lett.,89, 242114 (2006)

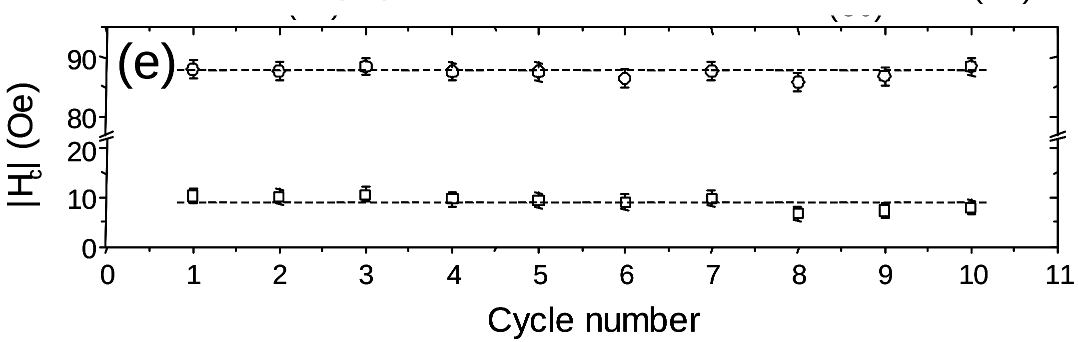
CoFeB//SiO_2







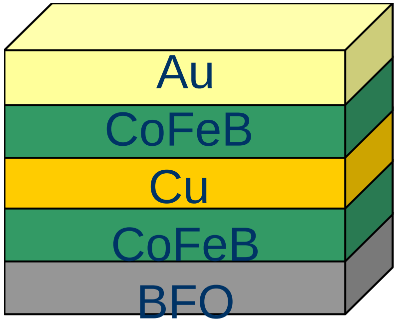


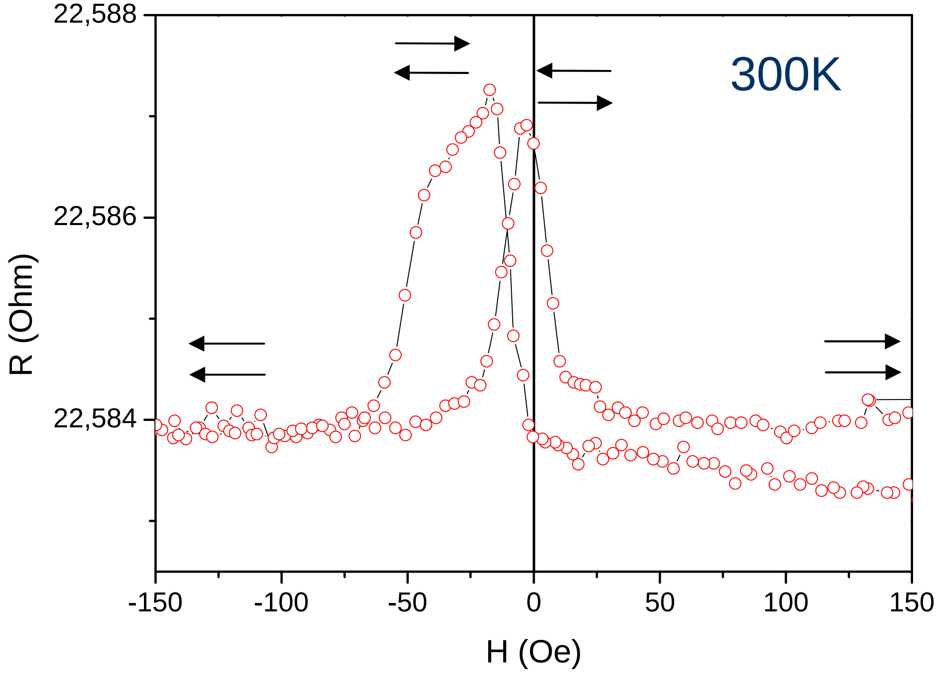


Robust room temperature exchange bias between BFO and CoFeB

With NiFe : **J. Dho et al., Adv. Mat., 18, 1445 (2006)**

Exchange bias with $BiFeO_3$ films

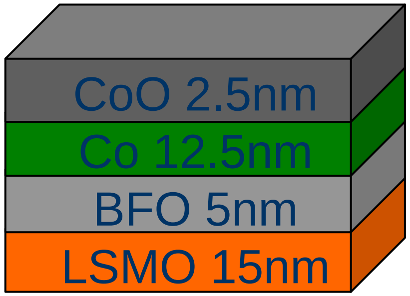


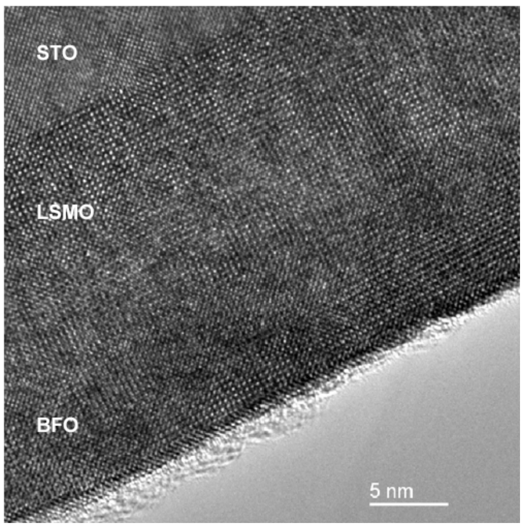


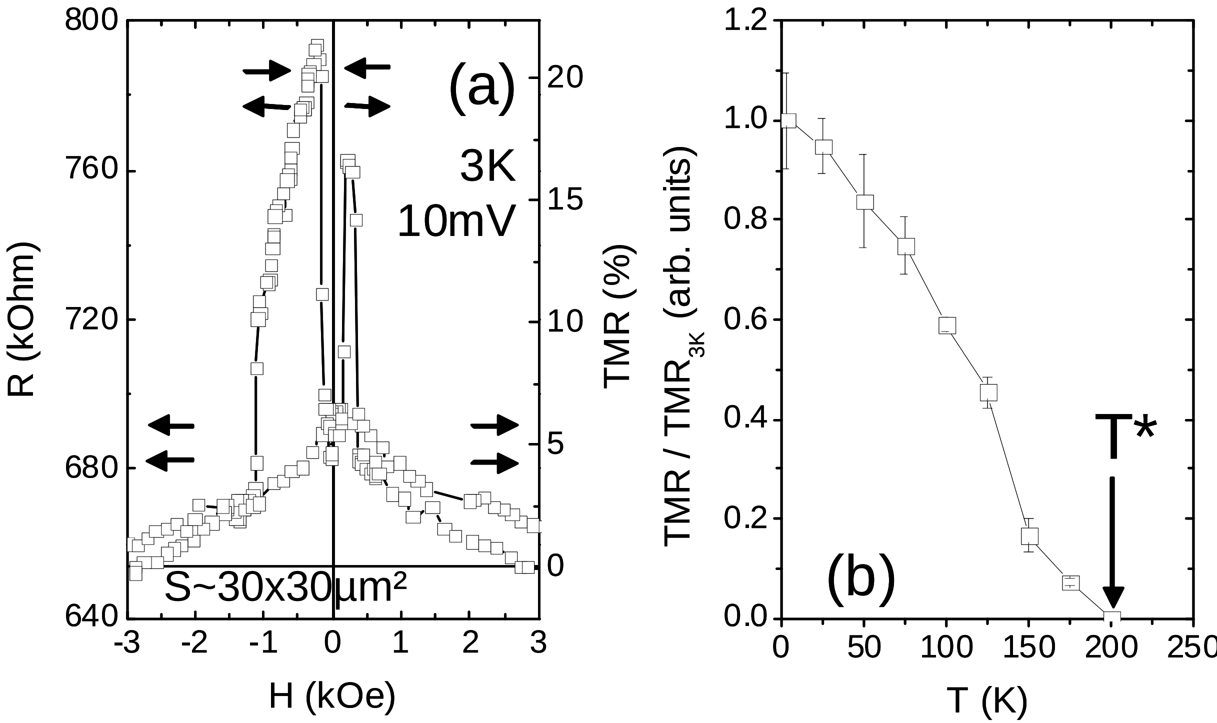
- ***GMR*** measured on top of BFO at RT
- ***Exchange bias*** has ***shifted*** the GMR curve

Tunnel junctions with $BiFeO_3$ barriers

O_2 growth pressure :
6.10^{-3} mbar
0.46 mbar







Appl. Phys. Lett., 89, 242114 (2006)

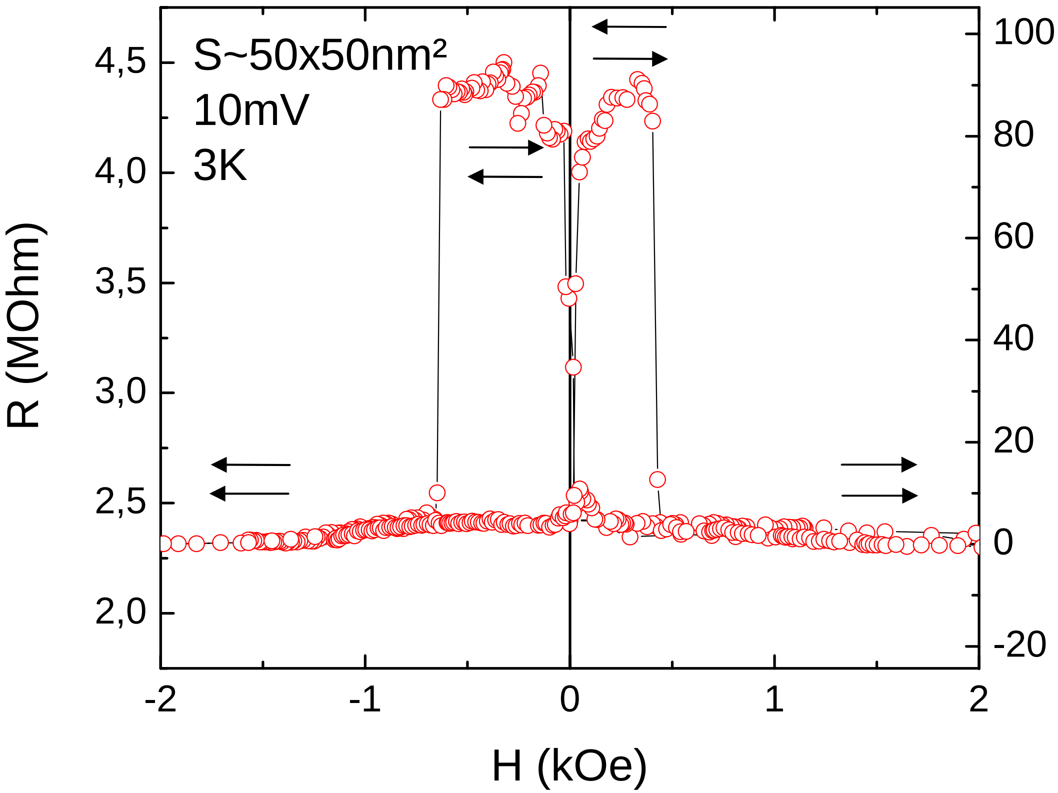
(exchange bias due to CoO, not to BFO)

Positive TMR up to ~30%

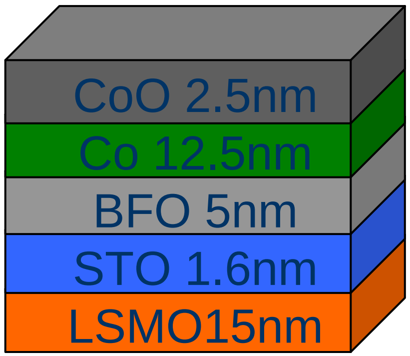
- rather large value for an AFM barrier
- positive spin polarization at Co/BFO interface

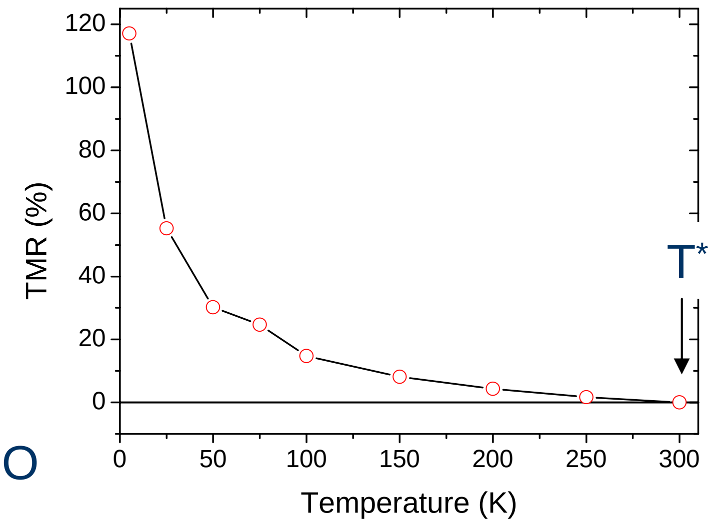
TMR vanishes around ***200K*** :
Local deoxygenation of LSMO

Tunnel junctions with $BiFeO_3$ barriers



O_2 growth pressure :
6.10^{-3} mbar
0.46 mbar
0.46 mbar

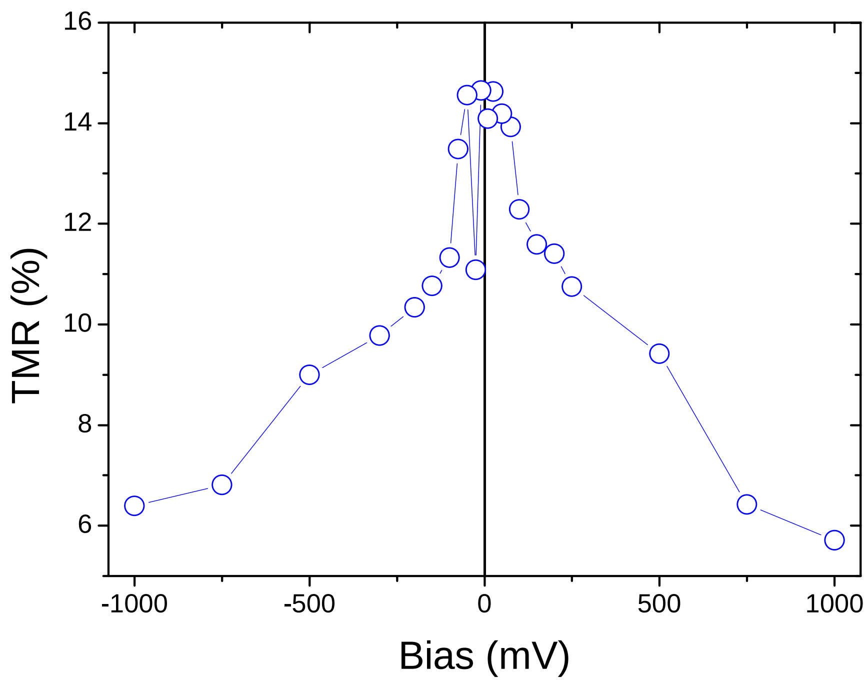


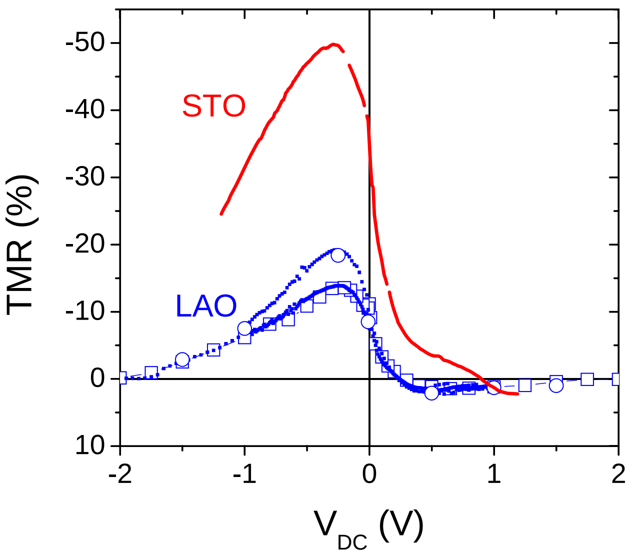


Positive TMR up to ~100%

- larger value than without STO
- polarization at Co/BFO interface still positive
- thanks to STO, better quality of the upper LSMO interface see **Appl. Phys. Lett., 82, 233 (2003)**

Tunnel junctions with $BiFeO_3$ barriers



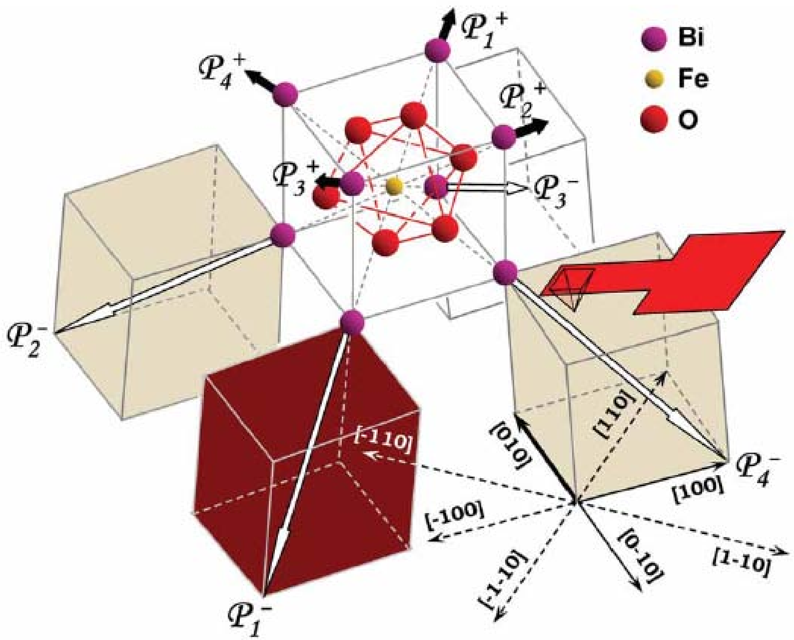


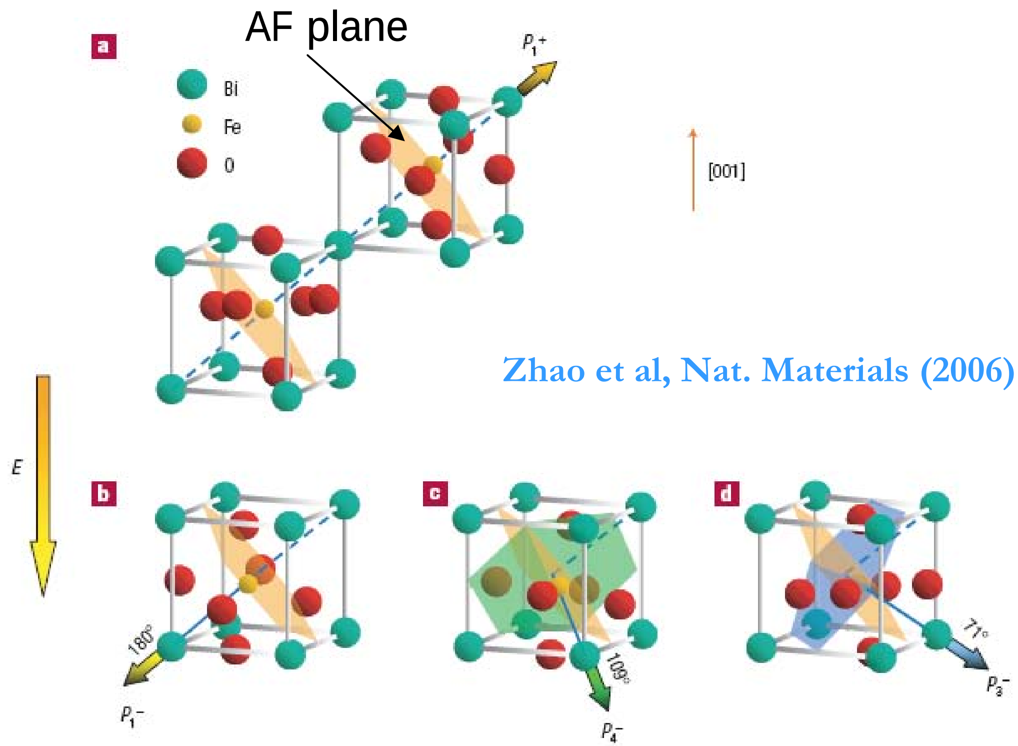
Bias dependence of TMR in LSMO/STO/Co and LSMO/LAO/Co junctions

Science 286, 507 (1999)
APL 87, 212501 (2005)

- TMR is positive and decreases symmetrically with bias voltage
- Behaviour is completely different from the case of LSMO/STO/Co and LSMO/LAO/Co junctions
- Possible reasons : oxygen vacancies at LSMO/BFO interface, symmetry filtering, etc

Domain structure and magnetoelectric switching





Zhao et al, Nat. Materials (2006)

P along <111> directions :
8 possible variants

When an electric field is applied, P can be switched to different directions
Only some of them yield a rotation of the AF plane

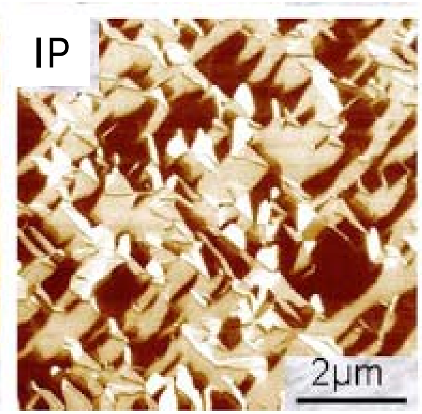
Important to know and control the ferroelectric domain structure

(001) $BiFeO_3$ films – Ferroelectric properties

Domain structure

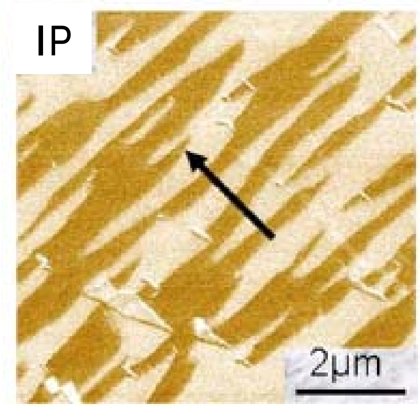
Piezoresponse force microscopy (PFM)

(001) film
0.8° miscut



8 variants are present

(001) film
4° miscut

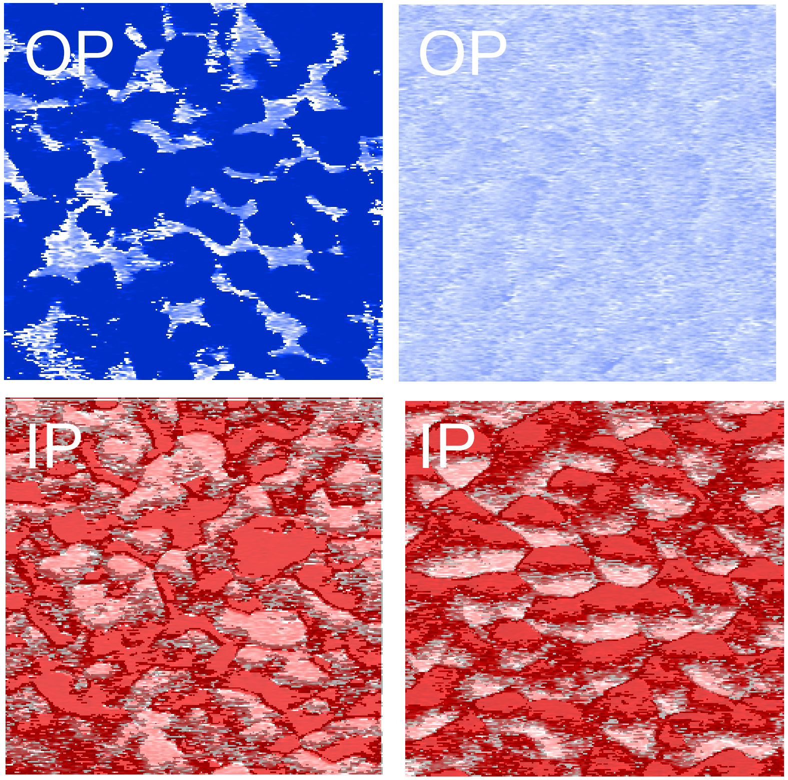


only 4 variants are present

Das et al., APL, 88, 242904 (2006)

Domain structure can be controlled by playing with the substrate miscut angle and/or orientation.

(001) films (111) films



8 variants are present

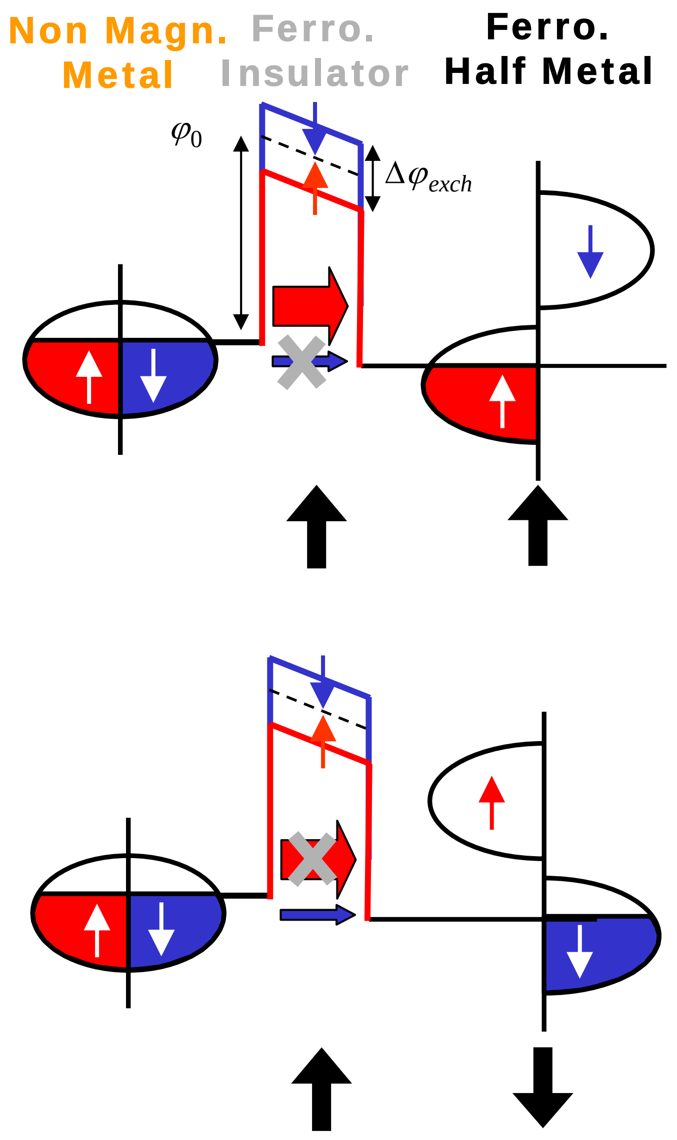
only 4 variants are present

Ideally, one type of domain orientation would be required, with the appropriate polarization switching mechanism (109° ?)

(La,Bi)MnO_3

A ferromagnetic ferroelectric

Ferromagnetic tunnel barriers: the spin-filter effect



Parallel Config.

large I, low R

Antiparallel Config.

low I, large R

Since the tunnel transmission depends exponentially on the barrier height, a highly-spin polarized current is generated by the barrier.

$$J_{\uparrow\downarrow} \propto e^{-(\varphi_0 \pm \frac{\Delta\varphi_{exch}}{2})^{1/2}}$$

Expected TMR :

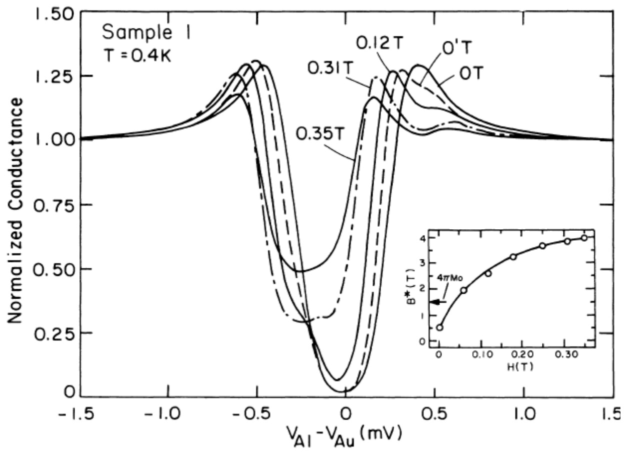
$$TMR = \frac{2P_E P_B}{1 - P_E P_B}$$

$$P_B = \frac{J_\uparrow - J_\downarrow}{J_\uparrow + J_\downarrow}$$

Ferromagnetic tunnel barriers

Spin-filters

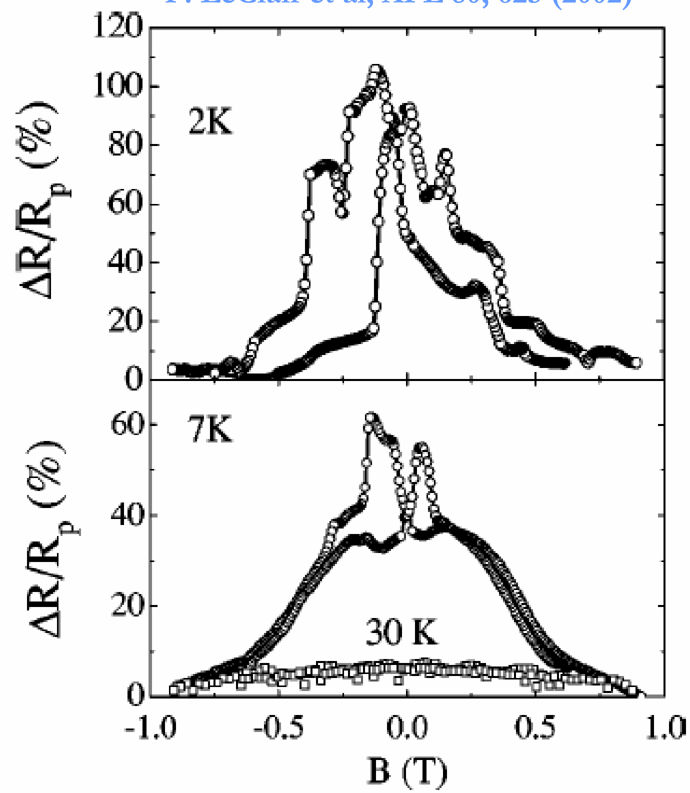
J.S. Moodera et al, PRB 42, 8235 (1990)



Au/EuS/Al spin-filter

Superconducting Al is used the spin-analyzer

P. LeClair et al, APL 80, 625 (2002)



Au/EuS/Gd spin-filter

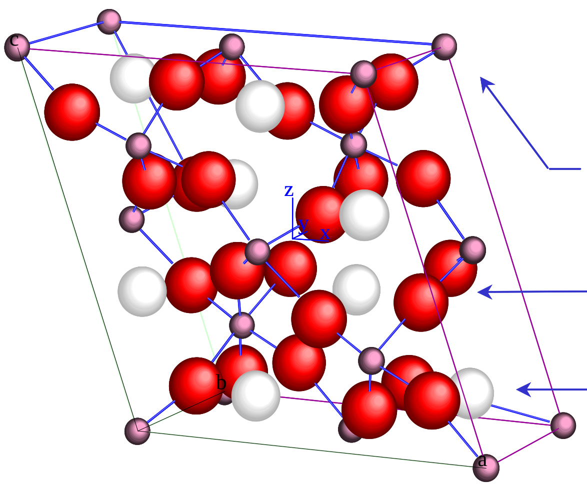
Ferromagnetic Gd is used as the spin-analyzer

- Early spin-filtering experiments focused on Eu chalcogenides
- Large spin-filtering efficiency (>90%) have been measured
- Limited by low Tc of EuX compounds

➔ **Ferromagnetic oxides**

$BiMnO_3$

Crystal structure



- Synthesis at high pressure
- Distorted perovskite structure (Monoclinic symmetry)
- Polar structure

→ Ferroelectric (?) Son et al, APL 84, 4971 (2004)

- « Magnetodielectric effect » observed in bulk samples

Kimura et al, PRB 67, 180401 (2003)

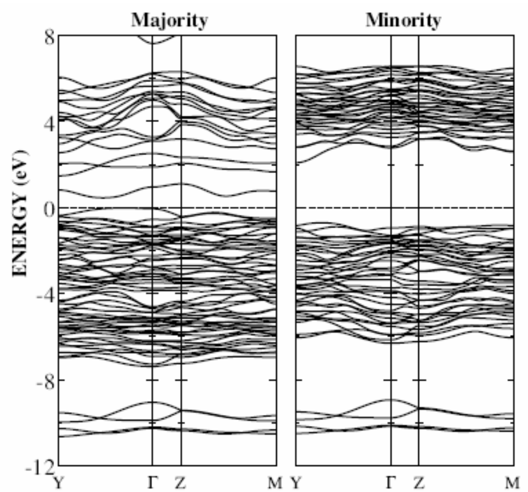
Magnetic ordering

- Unusual orbital ordering resulting from Bi_{6s}-O_{2p} interaction Moreira dos Santos et al, PRB 66 064425 (2002)

→ Ferromagnetic order

- T_C=105K, M_s=3.6 μ_B

Electronic structure



Ferromagnetic insulator with $E_{g\uparrow}$ = 0.5 eV and $E_{g\downarrow}$ = 2.6 eV

Shishidou et al, JPCM 2005

- Partial substitution of Bi by La : lower synthesis pressure, stabilization of perovskite phase

Troyanchuk et al, Low. Temp. Phys. 28, 569 (2002).

→ **Growth of $BiMnO_3$ and $La_{0.1}Bi_{0.9}MnO_3$ thin films**

$La_{1-x}Bi_xMnO_3$ thin films

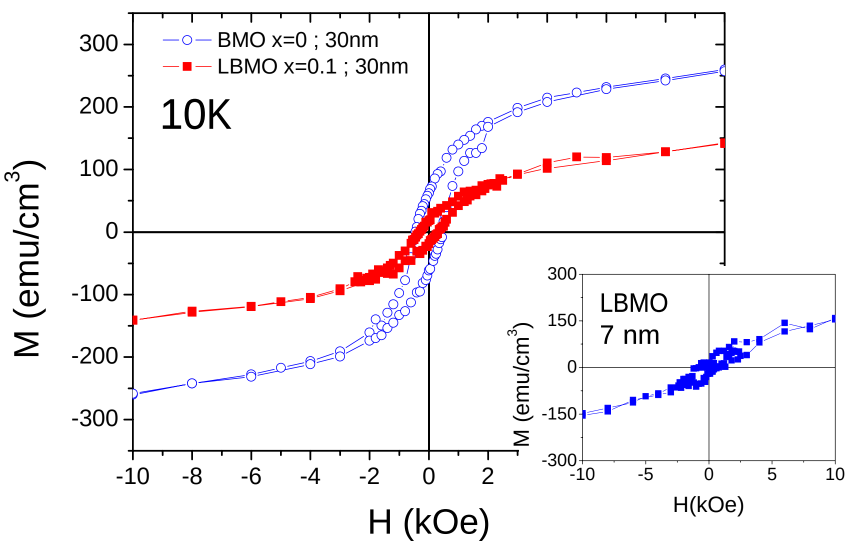
Growth by PLD

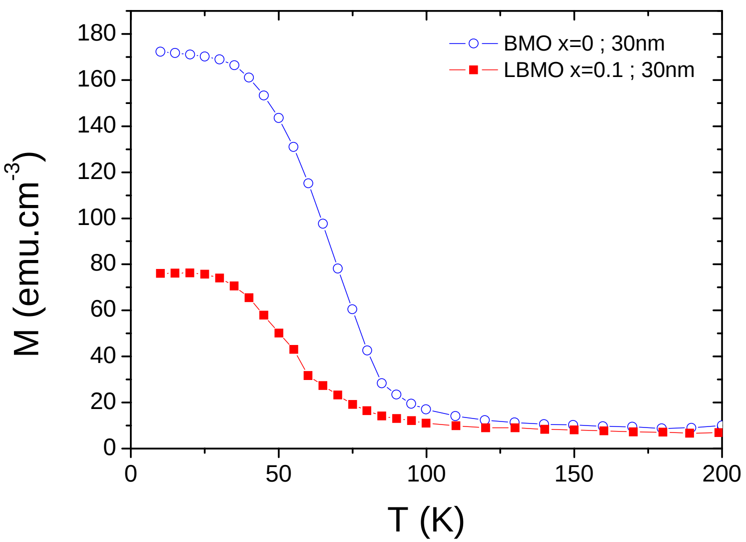
- KrF laser at 2 Hz
- Fluence: 2 J/cm².
- O_2 Pressure: 10^{-1} mbar.
- T_{dep} from 575°C to 700°C

Single phase films only in a very narrow window
La-substitution helps to stabilize the perovskite phase

See for details : **PRB 75, 174417 (2007)**
JAP 97 103909 (2005)

Magnetic properties





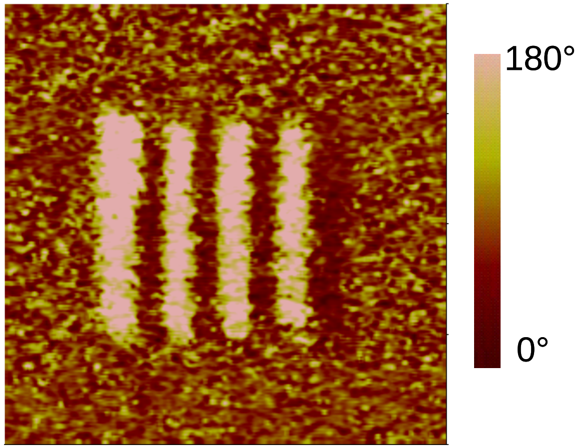
- BMO films have a reduced moment compared to bulk
- T_C close to bulk (105K)
- Substitution by La further reduces max. moment and slightly decreases T_C (as in bulk)
- Low magnetic moment likely due to Bi vacancies
- Very thin films are also ferromagnetic

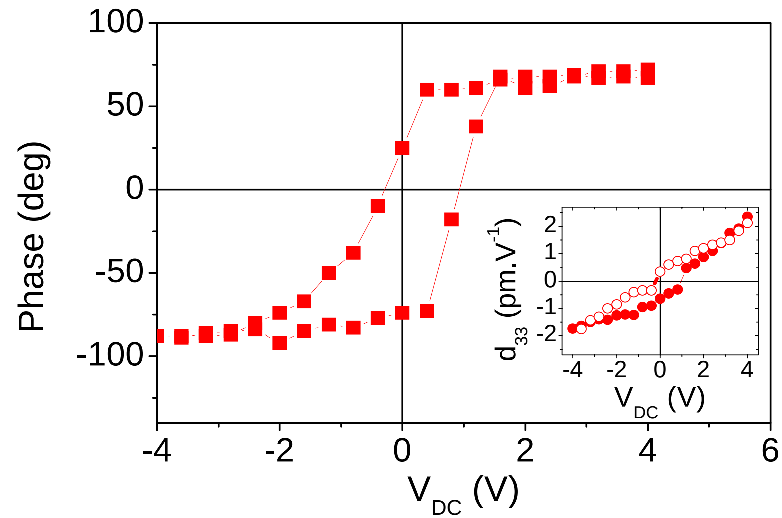
$La_{0.1}Bi_{0.9}MnO_3$ thin films

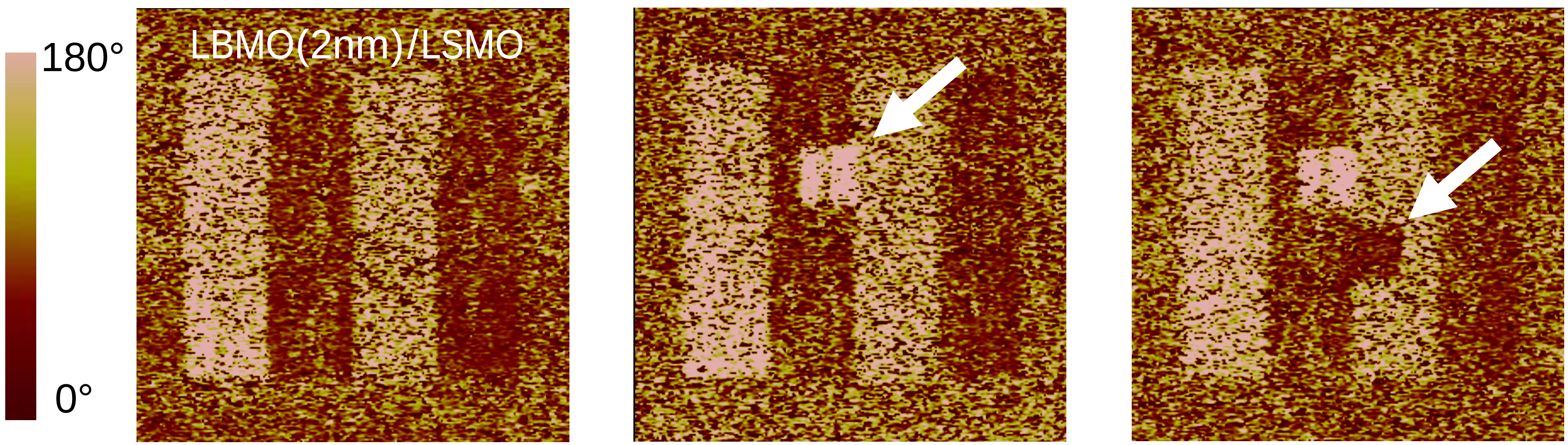
Ferroelectric properties

LBMO(30nm)/LSMO

PFM image after writing stripes at +/-4V







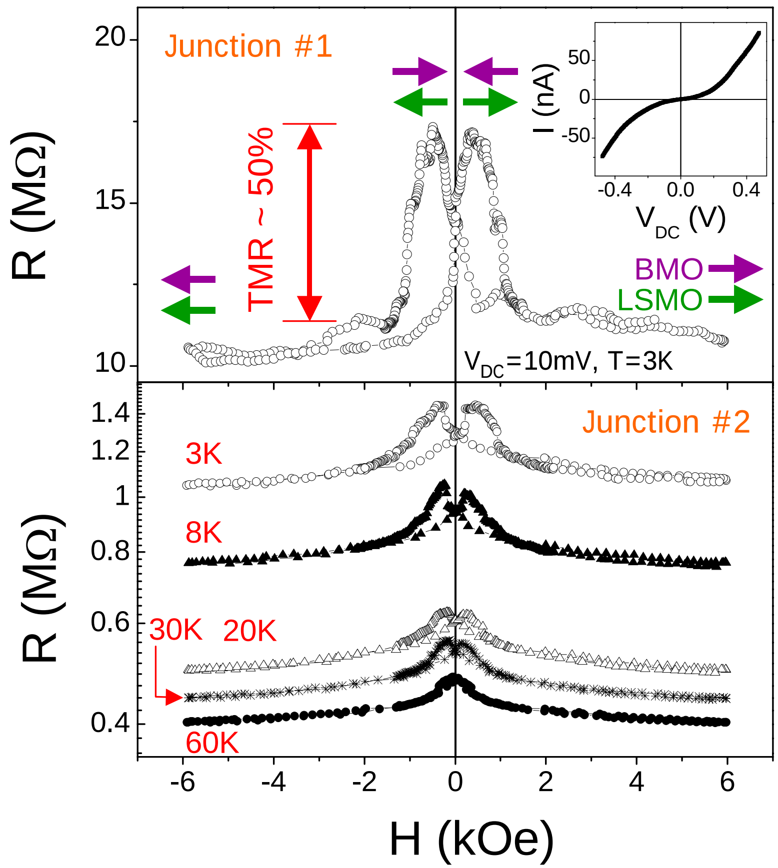
LBMO films as thin as 2 nm are still ferroelectric at room temperature

Nature Materials 6, 196 (2007)

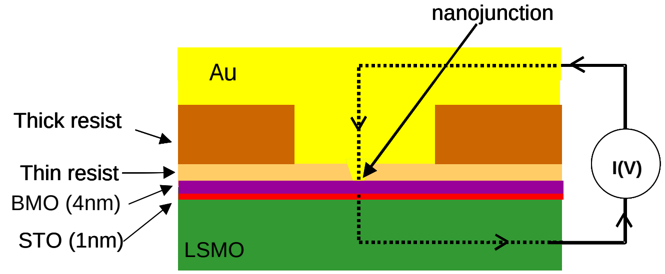
$BiMnO_3$-based junctions

Tunnel magnetoresistance

LSMO / STO (1 nm) / BMO (4 nm) / Au



PRB 72 020406(R) (2005)



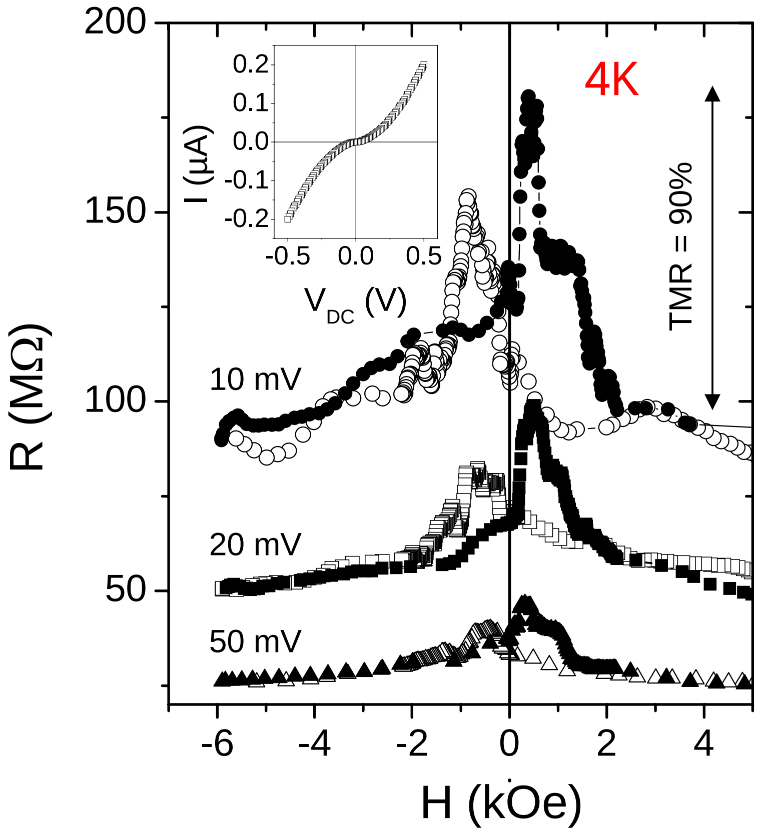
Junctions defined by nano-indentation lithography

Nanoletters 3, 1599 (2003)

- Large TMR at low temperature
  ➔ spin-filtering by the BMO layer
- Polarization induced by BMO : **22%**
- Spin-filter effect vanishes at T < T_C

Tunnel magnetoresistance

LSMO / STO (1 nm) / LBMO (4 nm) / Au



JAP 99, 08E504 (2006)

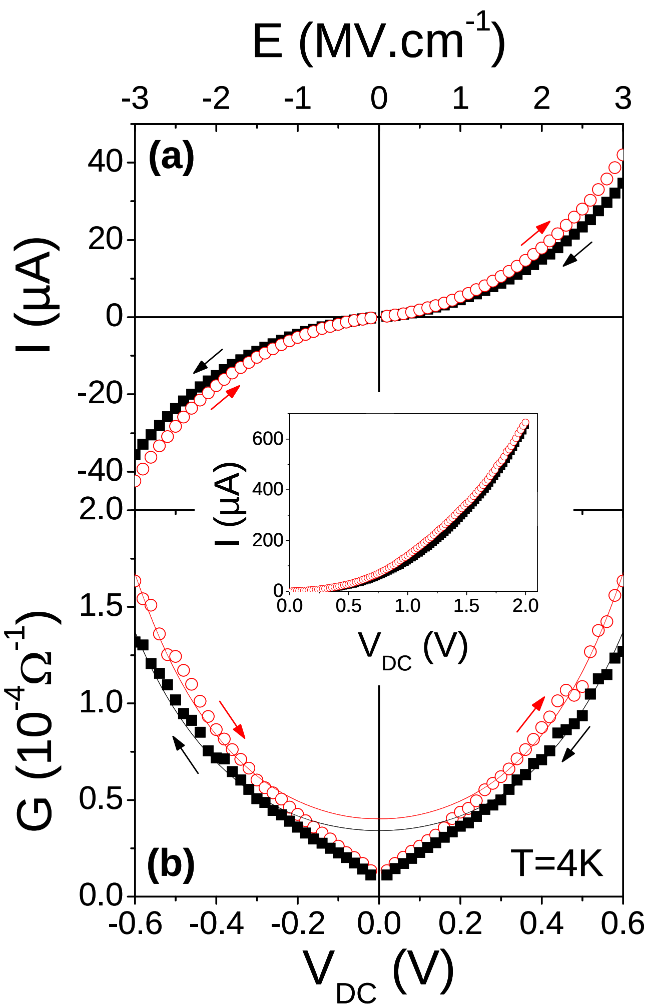
- Polarization induced by LBMO : **35 %**
- TMR decreases rapidly with bias

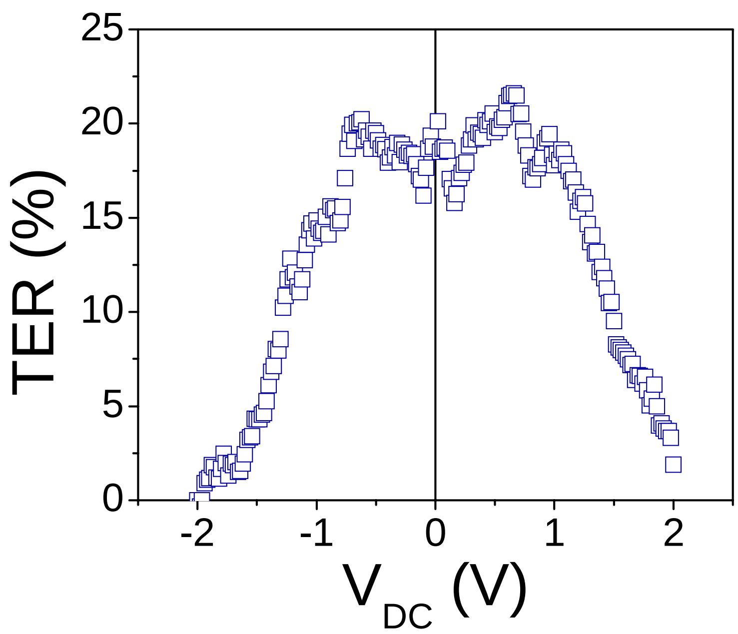
Magnons ? Defects ?

LBMO-based junctions

Tunnel electroresistance

LSMO / LBMO (2 nm) / Au



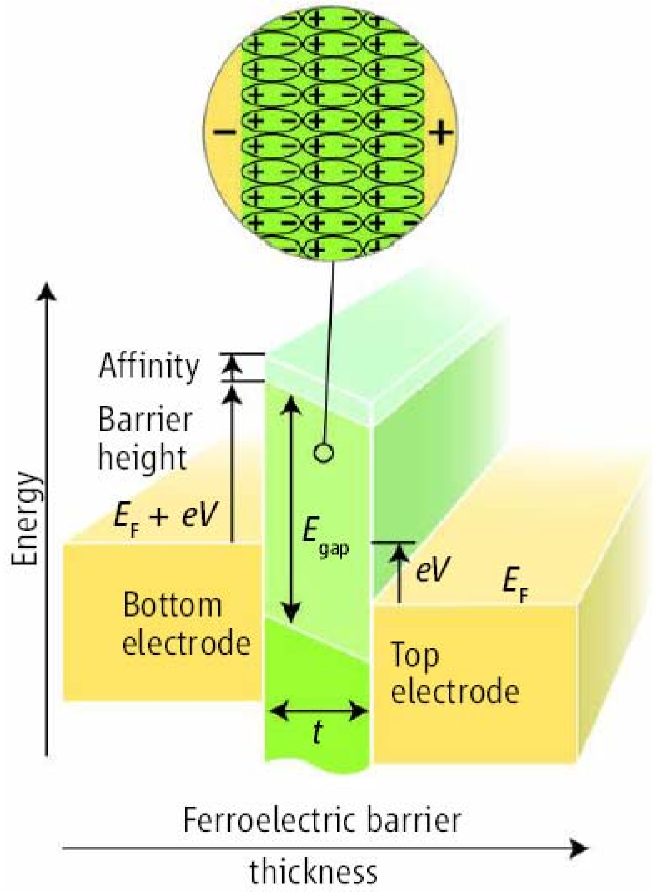


- A ~20% electroresistance effect is observed
- The shape of the G(V) curve suggests direct tunneling

What is the origin of the TER ?

Nature Materials 6, 196 (2007)

Tunneling through a ferroelectric tunnel barrier

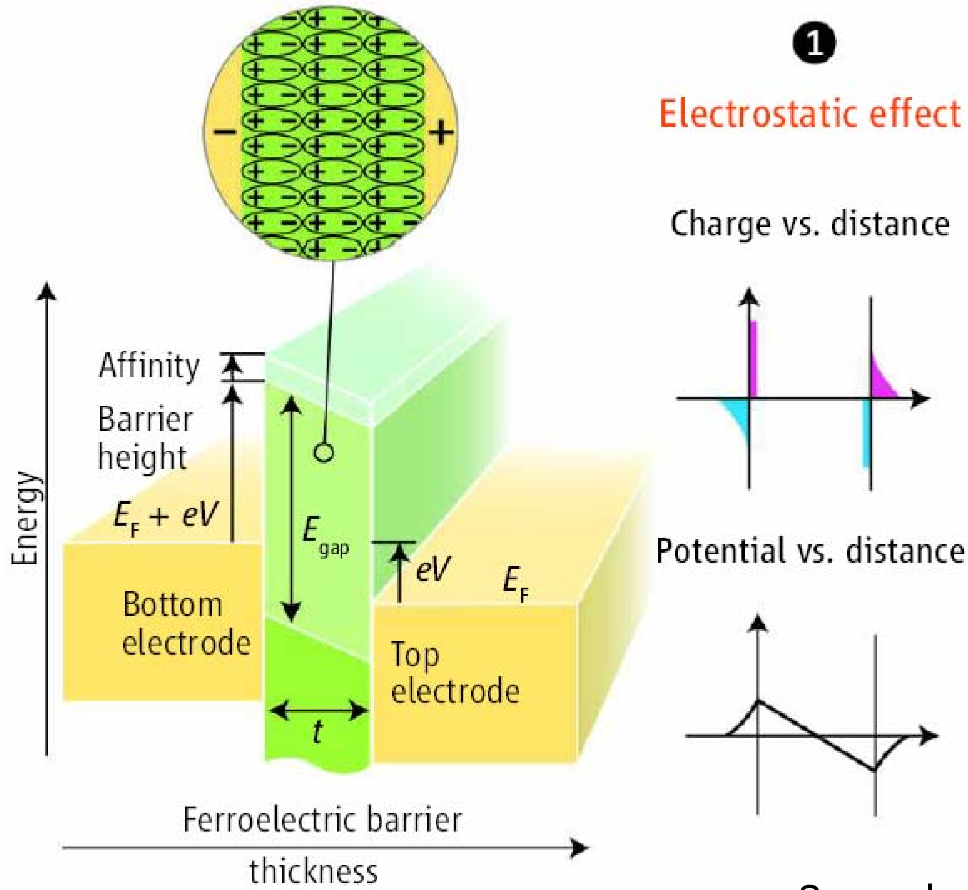


From Tsymbal and Kohlstedt
Science 313, 181 (2006)

Several mechanisms leading to current modulation upon polarization reversal

Ferroelectric tunnel barriers

Tunneling through a ferroelectric tunnel barrier



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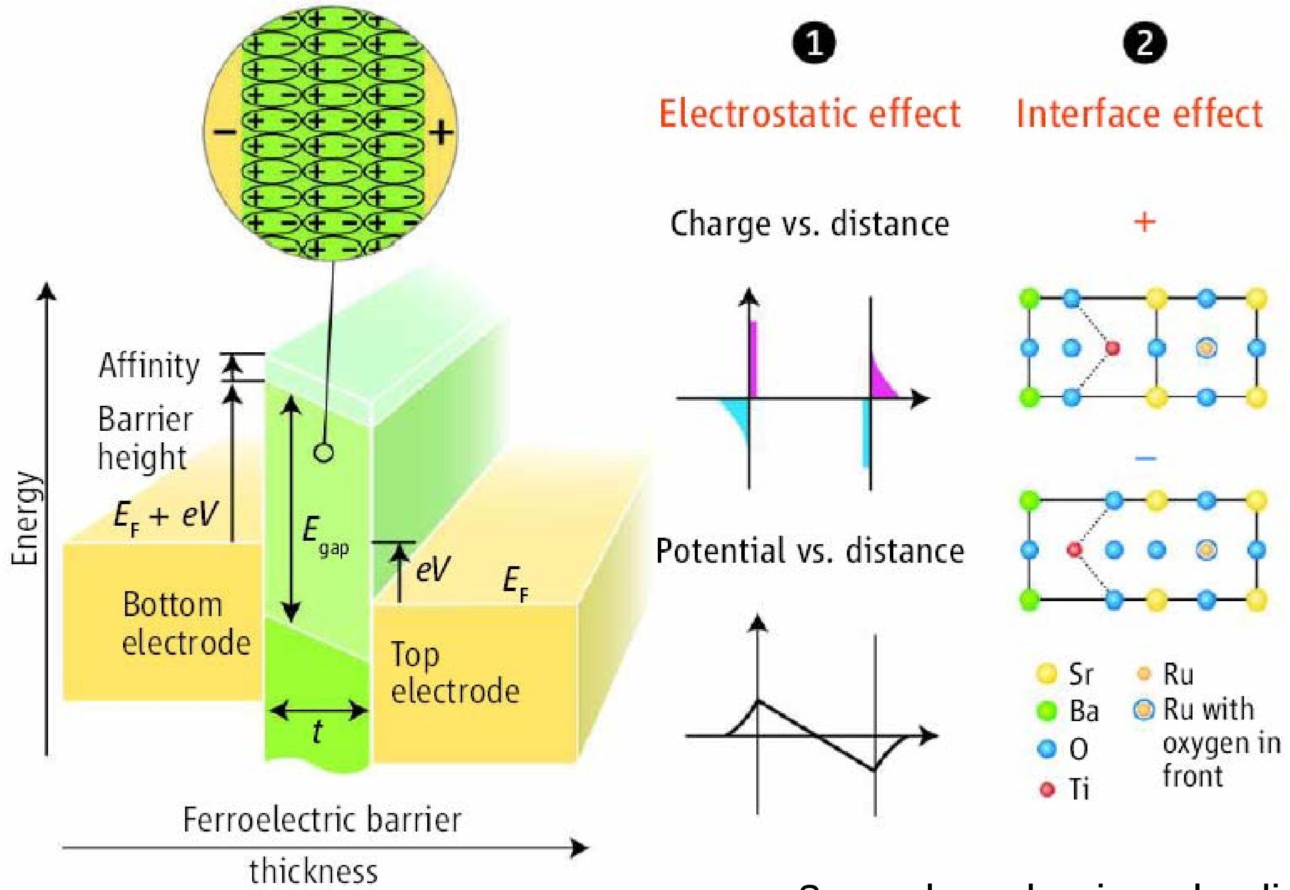

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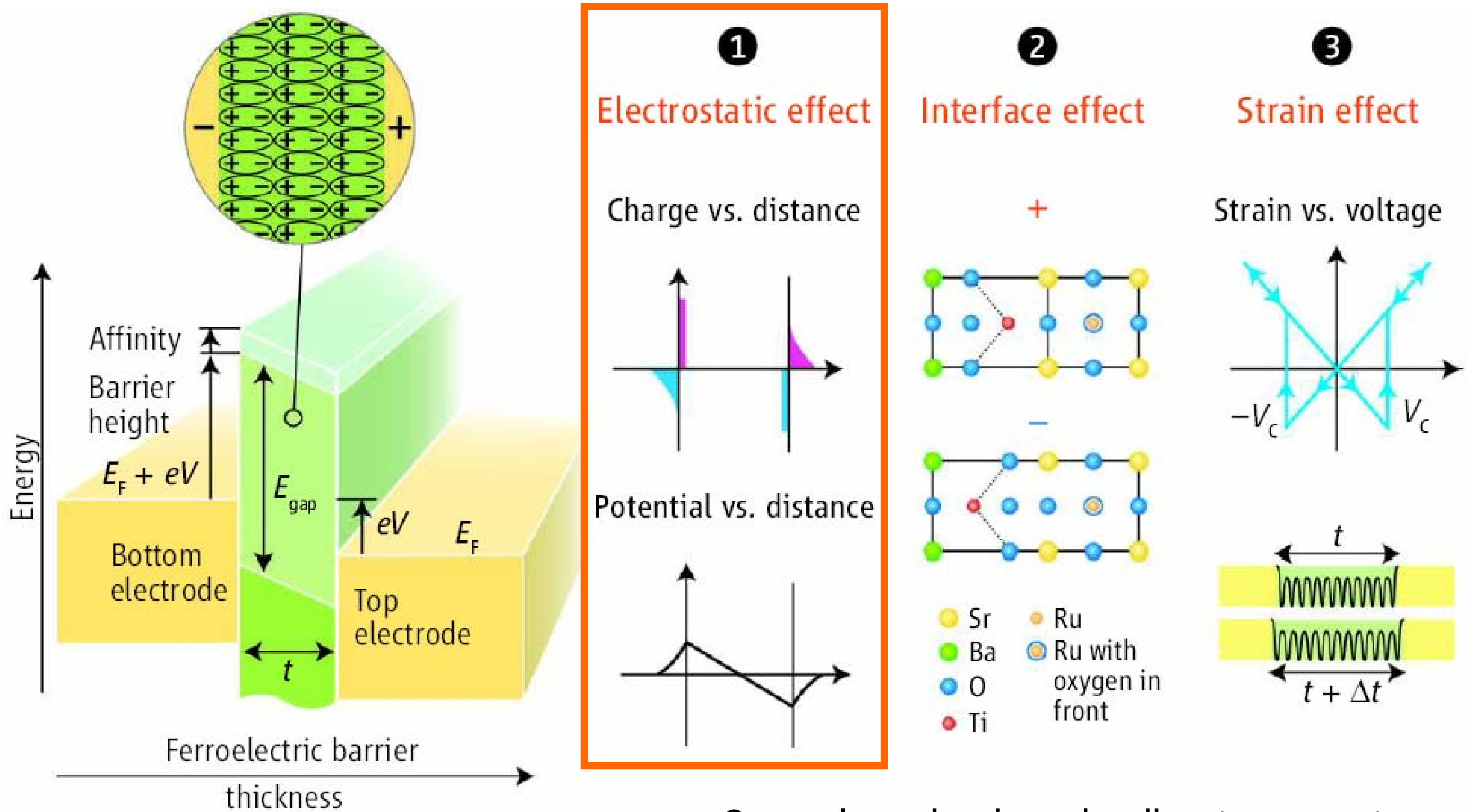

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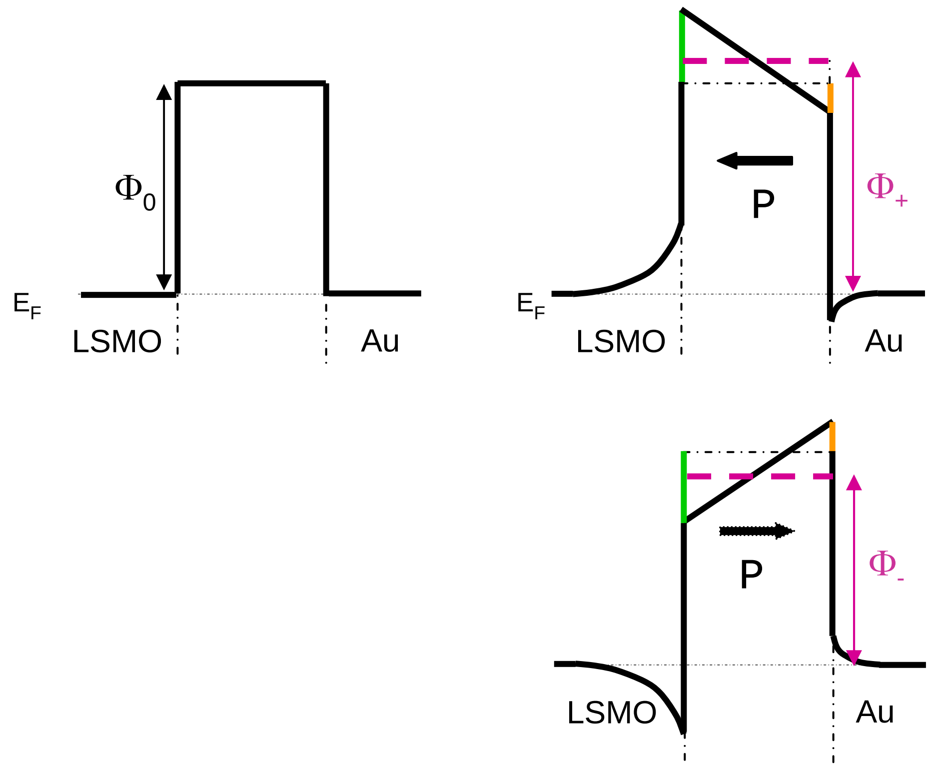


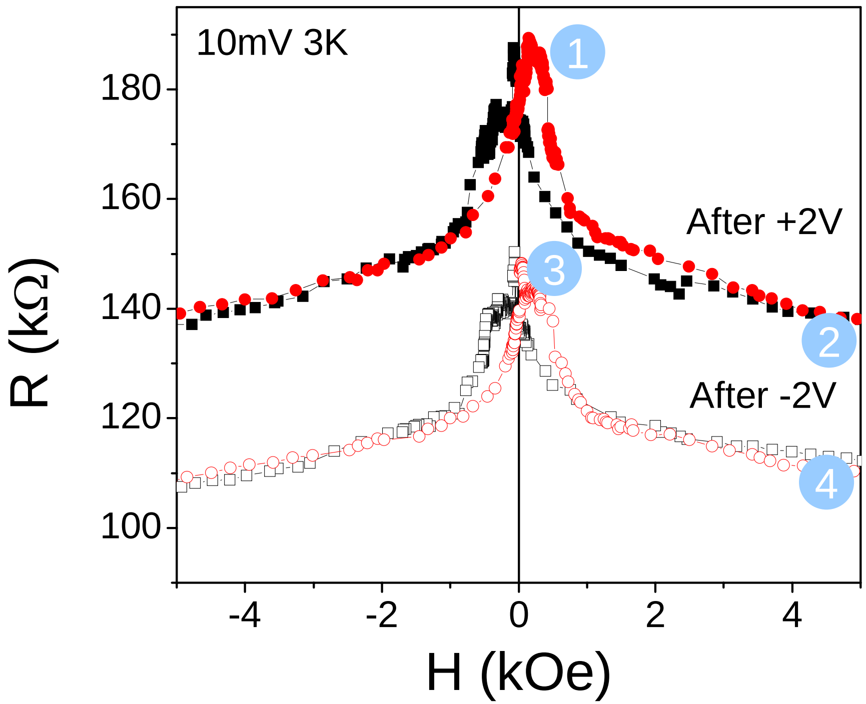
Large average barrier height
➔ low tunnel current

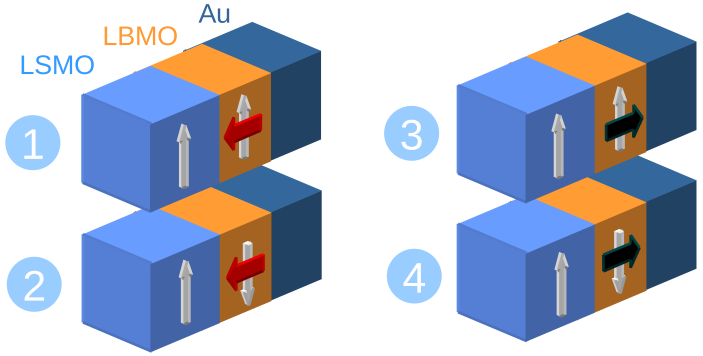
Low average barrier height
➔ large tunnel current

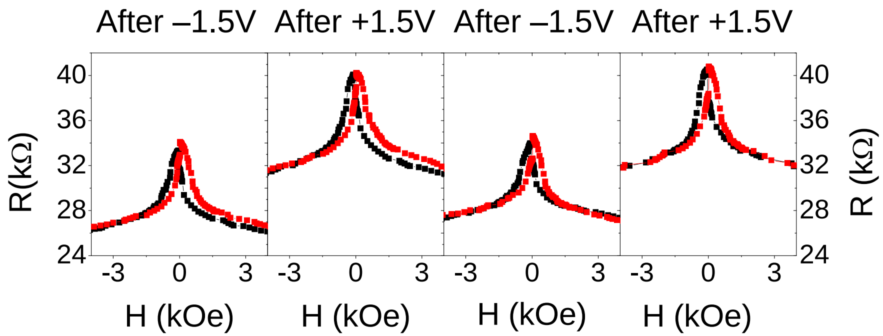
Hysteretic I(V) curves are expected
An electroresistance effect should occur upon polarization reversal

See details in Zhuravlev et al, PRL 94, 246802 (2005)

Combination of tunnel electroresistance and magnetoresistance



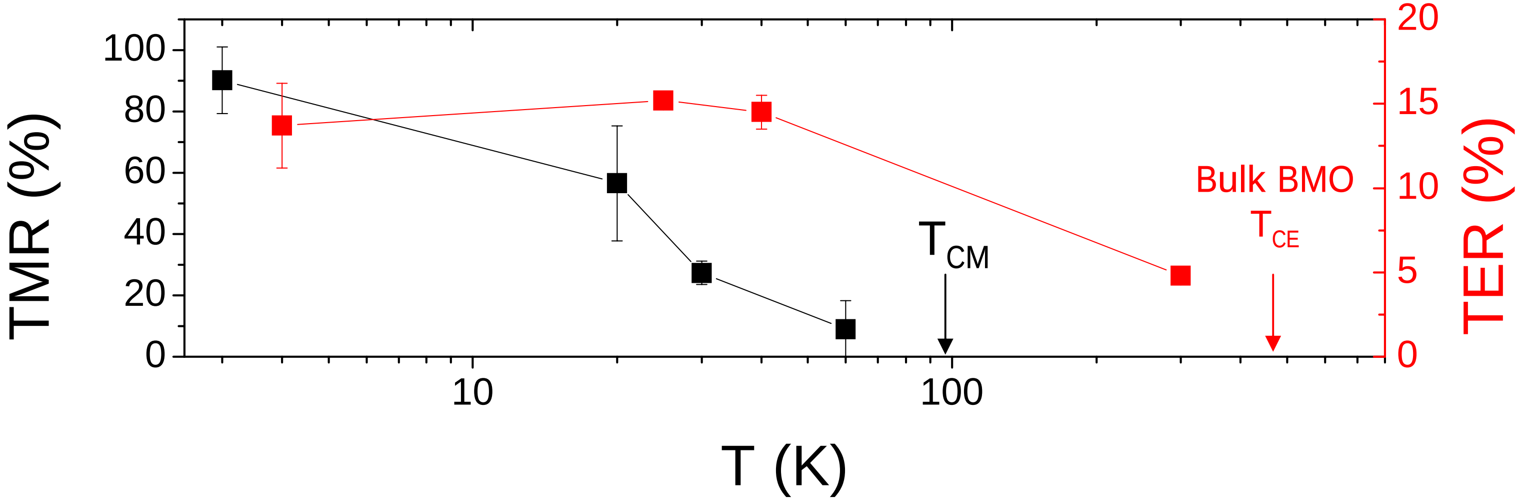




- Demonstration of a 4-resistance state system with a multiferroic barrier
- Effect was observed on several junctions and is reproducible

Nature Materials 6, 196 (2007)

Temperature dependence of TER and TMR



Temperature dependence of TER and TMR consistent with an origin related to to ferroelectricity and ferromagnetism, respectively

Conclusions and perspectives

$BiFeO_3$

Single phase films can be grown in a narrow range of P and T
They are G-type antiferromagnetic and ferroelectric at RT
LSMO/BFO/Co junctions show a large positive TMR
BFO induced exchange bias on CoFeB

$(La,Bi)MnO_3$ based junctions

$La_{0.1}Bi_{0.9}MnO_3$ films are ferromagnetic and ferroelectric
LBMO junctions show TMR and electroresistance (4 resistance states)
We suggest electroresistance effect due to ferroelectric switching in the barrier
Control of the magnetic state by electric field ?

Perspectives :
Magnetization manipulation with an electric field at RT
New materials, ideally ferromagnetic multiferroics with high T_Cs, M_S and P are required

See review on Oxide Spintronics by M. Bibes and A. Barthélémy, IEEE Trans. Electron Devices 54, 1003 (2007)

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