

# Matériaux fonctionnels en couches minces : dépôts physiques en phase vapeur

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# Apport des couches minces en Chimie du Solide

utilisation des propriétés du massif dans des dispositifs – applications

nouvelles propriétés par réduction des dimensions – effets d'échelle

nouvelles propriétés par contraintes – effet du substrat

nouvelles fonctionnalités par couplage

# Les différentes approches

Approche « top-down »      les enjeux sociétaux

Energie

Environnement

Technologies de l'information

Approche « bottom-up »      et sérendipité

Nouveaux matériaux

Nouvelles fonctionnalités

# Des matériaux de choix : les oxydes

## Interface Physics in Complex Oxide Heterostructures

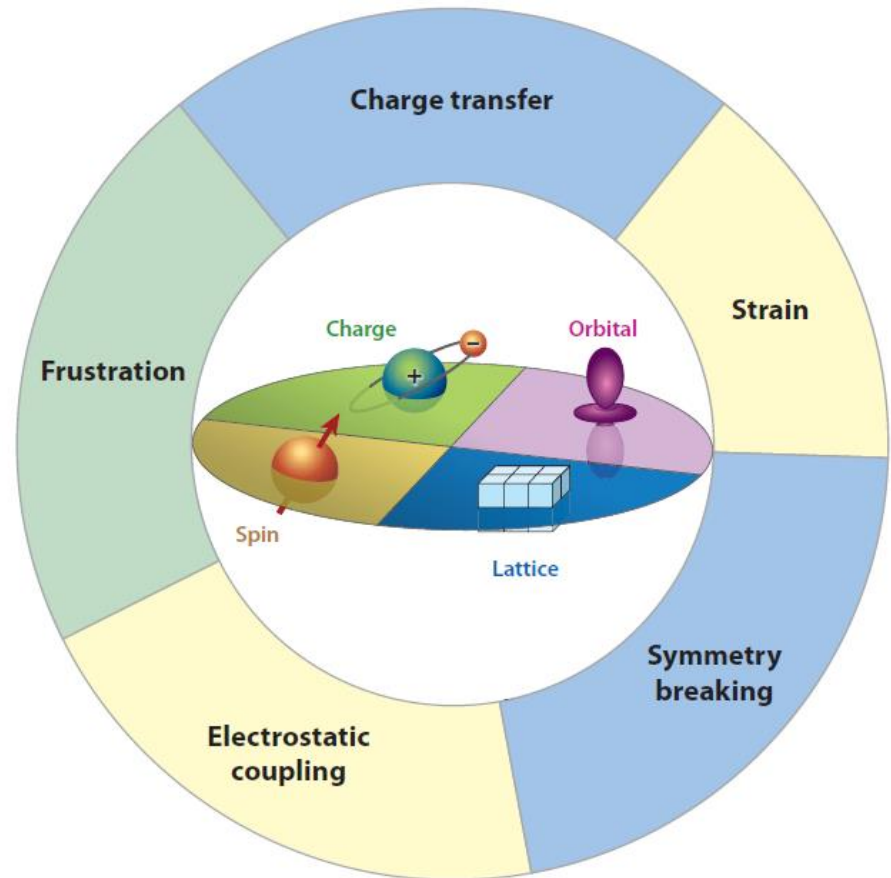
Pavlo Zubko,<sup>1</sup> Stefano Gariglio,<sup>1</sup> Marc Gabay,<sup>2</sup>  
Philippe Ghosez,<sup>3</sup> and Jean-Marc Triscone<sup>1</sup>

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Riche palette d'effets physiques



[Zubko *et al.* *Ann. Rev. Condens. Matter Phys.*  
2 (2011) 141-65]

# Les méthodes de dépôt

## Voies chimiques

Sol-gel

Chemical Vapor Deposition

Atomic Layer Deposition

...

## Voies physiques

Pulvérisation cathodique

Ablation laser

Epitaxie par jet moléculaire

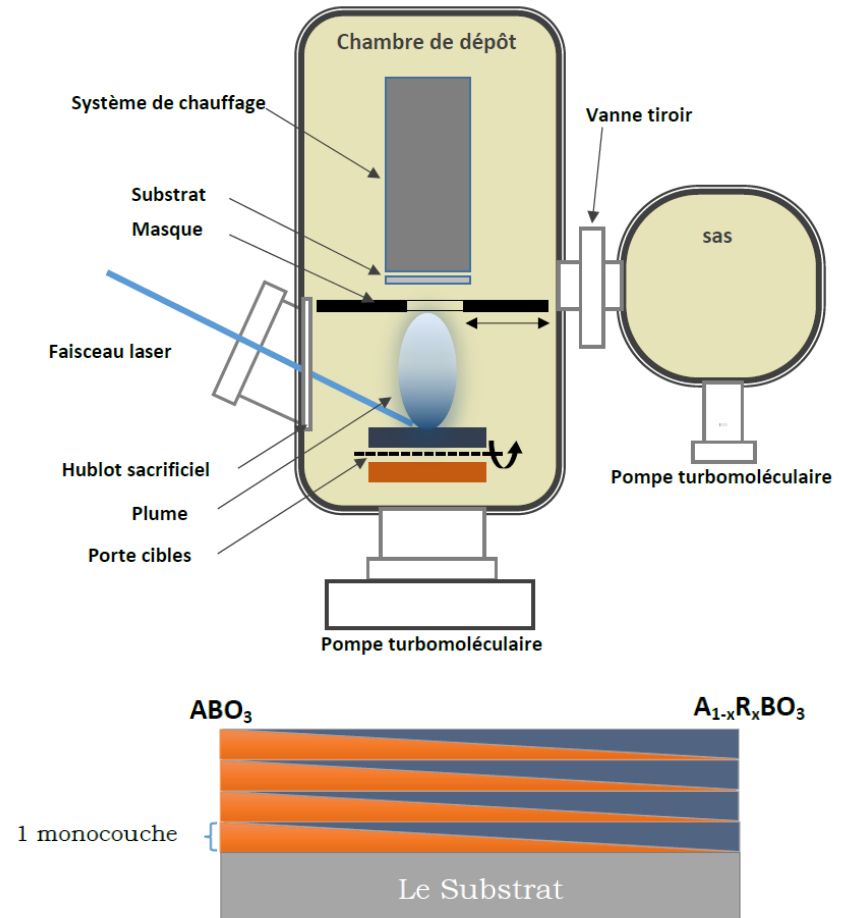
...

# Les techniques de dépôt : quelques particularités

## Ablation laser combinatoire



GREMAN, Tours



# Les techniques de dépôt : quelques particularités

## Epitaxie combinatoire

JOURNAL OF APPLIED PHYSICS **118**, 045306 (2015)



### Preferential orientation relationships in $\text{Ca}_2\text{MnO}_4$ Ruddlesden-Popper thin films

M. Lacotte,<sup>1</sup> A. David,<sup>1</sup> G. S. Rohrer,<sup>2</sup> P. A. Salvador,<sup>2</sup> and W. Prellier<sup>1,a)</sup>

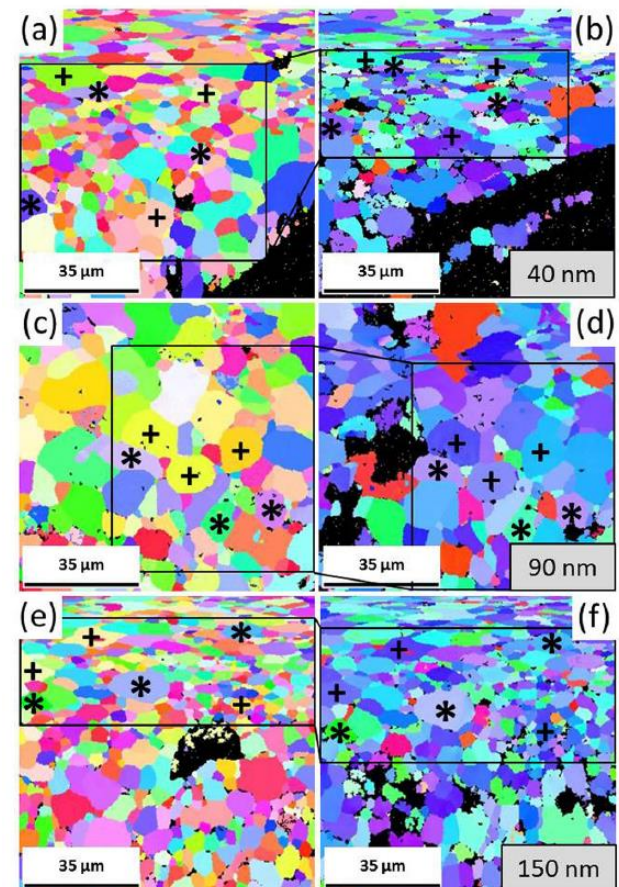
<sup>1</sup>Laboratoire CRISMAT, CNRS UMR 6508, ENSICAEN, Université de Basse-Normandie, 6 Bd Maréchal Juin, F-14050 Caen Cedex 4, France

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(Received 20 March 2015; accepted 16 July 2015; published online 28 July 2015)

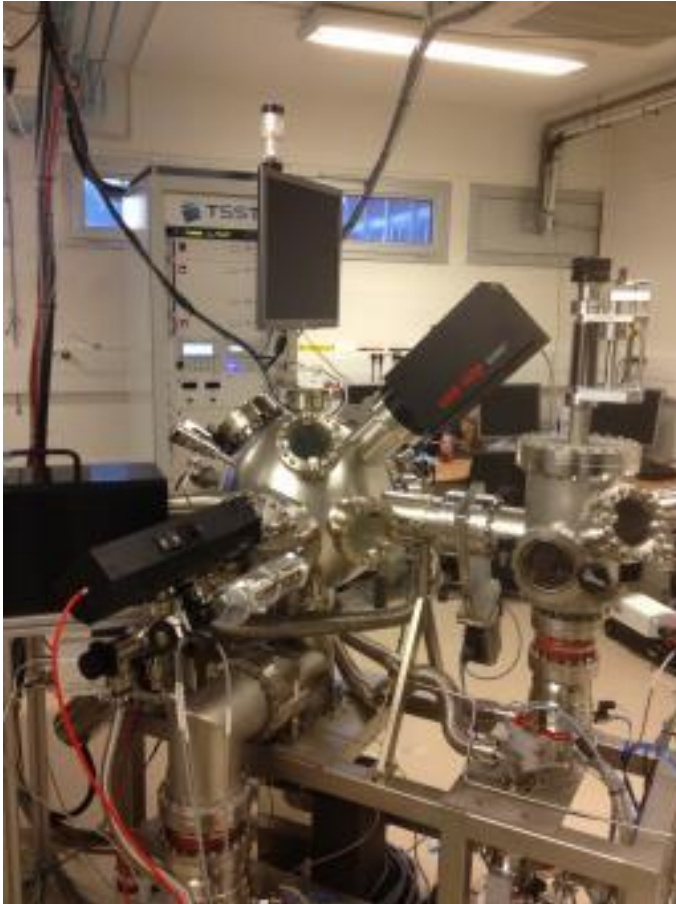
A high-throughput investigation of local epitaxy (called combinatorial substrate epitaxy) was carried out on  $\text{Ca}_2\text{MnO}_4$  Ruddlesden-Popper thin films of six thicknesses (from 20 to 400 nm), all deposited on isostructural polycrystalline  $\text{Sr}_2\text{TiO}_4$  substrates. Electron backscatter diffraction revealed grain-over-grain local epitaxial growth for all films, resulting in a single orientation relationship (OR) for each substrate-film grain pair. Two preferred epitaxial ORs accounted for more than 90% of all ORs on 300 different microcrystals, based on analyzing 50 grain pairs for each thickness. The unit cell over unit cell OR ( $[100][001]_{\text{film}} \parallel [100][001]_{\text{substrate}}$ , or OR1) accounted for approximately 30% of each film. The OR that accounted for 60% of each film ( $[100][001]_{\text{film}} \parallel [100][010]_{\text{substrate}}$ , or OR2) corresponds to a rotation from OR1 by  $90^\circ$  about the a-axis. OR2 is strongly favored for substrate orientations in the center of the stereographic triangle, and OR1 is observed for orientations very close to (001) or to those near the edge connecting (100) and (110). While OR1 should be lower in energy, the majority observation of OR2 implies kinetic hindrances decrease the frequency of OR1. Persistent grain over grain growth and the absence of variations of the OR frequencies with thickness implies that the growth competition is finished within the first few nm, and local epitaxy persists thereafter during growth. © 2015 AIP Publishing LLC.

[<http://dx.doi.org/10.1063/1.4927518>]



# Les techniques de dépôt : quelques particularités

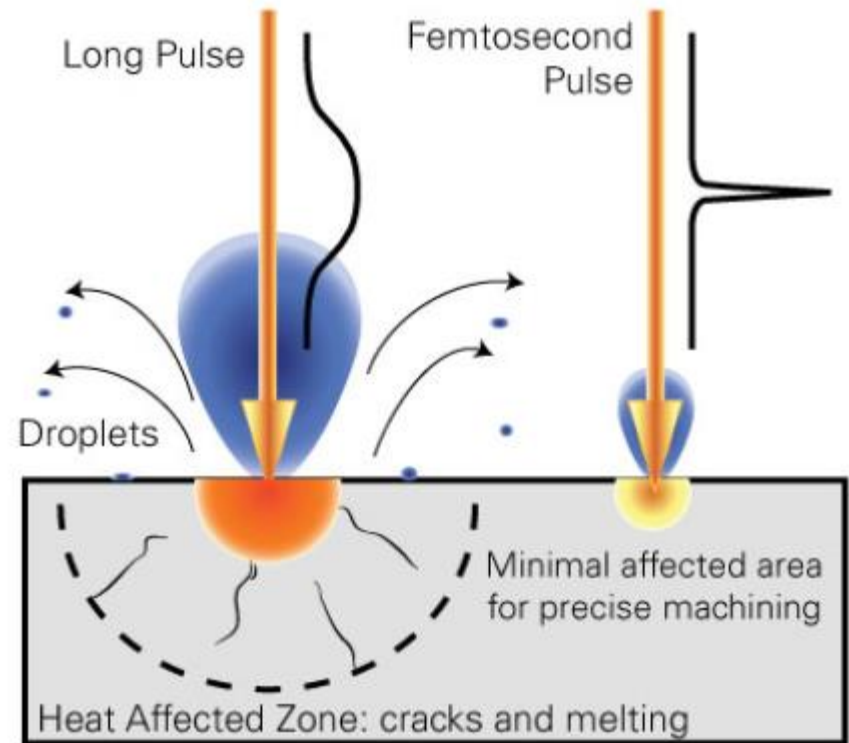
## PLD femtoseconde



Laser fs  
( $t = 100 \text{ fs}$  /  $\lambda = 800 \text{ nm}$  /  $f = 1 \text{ kHz}$  /  $P_{\text{max}} = 4 \text{ W}$ )

CEA-SPEC Saclay

ANF Chimie du solide, Caen, 23-25 novembre 2015



temps d'interaction court  
processus d'interaction simplifié  
déjà utilisé pour la gravure mais pas  
encore pour dépôt de couches)



# Les techniques de dépôt : quelques particularités

## MBE oxydes

APL MATERIALS 3, 062403 (2015)

### Perspective: Oxide molecular-beam epitaxy rocks!

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(Received 13 March 2015; accepted 20 April 2015; published online 26 May 2015)

Molecular-beam epitaxy (MBE) is the “gold standard” synthesis technique for preparing semiconductor heterostructures with high purity, high mobility, and exquisite control of layer thickness at the atomic-layer level. Its use for the growth of multicomponent oxides got off to a rocky start 30 yr ago, but in the ensuing decades, it has become the definitive method for the preparation of oxide heterostructures too, particularly when it is desired to explore their intrinsic properties. Examples illustrating the unparalleled achievements of oxide MBE are given; these motivate its expanding use for exploring the potentially revolutionary states of matter possessed by oxide systems. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4919763>]

Des spécificités techniques : source d'oxydation  
oxygène moléculaire, ozone, ozone distillé

# Les techniques de dépôt : quelques particularités

## MBE oxydes en France



CEA IRAMIS Saclay

oxydation par plasma d'oxygène  
monoatomique



Institut Jean Lamour, Nancy

générateur d'ozone

# Les besoins spécifiques en caractérisations

## Propriétés physiques

Propriétés optiques, magnétiques

- MOKE, SQUID, Spectroscopie ellipsométrique, ...

Propriétés électriques

- mesures macroscopiques – nécessitent lithographie, courants de fuite
- mesures par sondes locales (TUNA, PFM, ...) – attention aux artefacts
- mesures synchrotron

## Structure

La maille et la position des atomes dans la maille

diffraction X, microscopie électronique par précession des électrons

La distribution cationique

XMCD, spectrométrie Mössbauer, XPS, diffraction X résonante

# Les besoins spécifiques en caractérisation

## Détermination structurale - Position des atomes

## Structural analysis of strained $\text{LaVO}_3$ thin films

H Rotella<sup>1,5</sup>, O Copie<sup>1,6</sup>, G Steciuk<sup>1</sup>, H Ouerdane<sup>1,7</sup>, P Boullay<sup>1</sup>,  
P Roussel<sup>2</sup>, M Morales<sup>3</sup>, A David<sup>1</sup>, A Pautrat<sup>1</sup>, B Mercey<sup>1</sup>, L Lutterotti<sup>4</sup>,  
D Chateigner<sup>1</sup> and W Prellier<sup>1</sup>

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<sup>2</sup> Laboratoire UCCS, CNRS UMR 8181, ENSCL, Bat C7, BP 90108 F-59652 Villeneuve d'Ascq, France

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Diffraction des rayons X  
(type monocristal)

Confirmation Microscopie  
Electronique en Transmission :  
Précession des électrons  
(Precession Electron Diffraction)

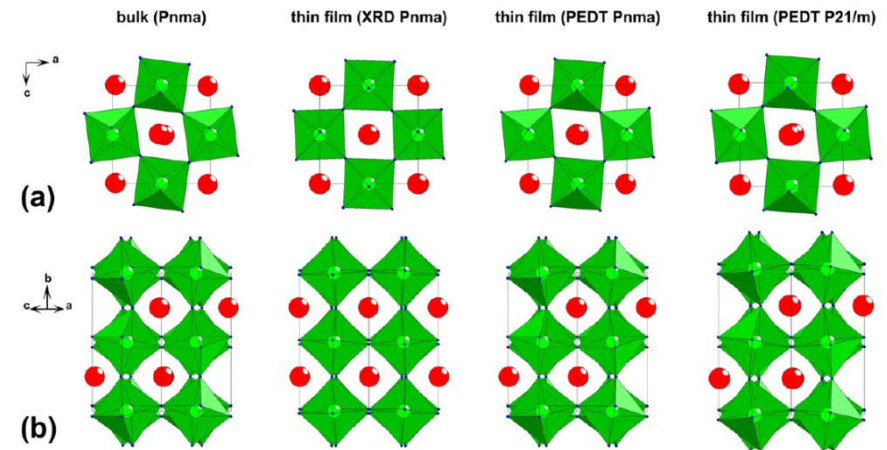


Figure 6. Schematic representation of the structure of bulk LVO (room temperature) [19] and LVO thin films as obtained from XRD and PEDT refinements. (a) [010] projection (b) [101] projection.

# Les besoins spécifiques en caractérisation

## Détermination structurale – Distribution cationique

Journal of Electron Spectroscopy and Related Phenomena 202 (2015) 16–21

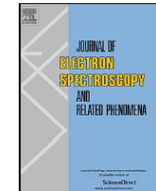


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Journal of Electron Spectroscopy and  
Related Phenomena

journal homepage: [www.elsevier.com/locate/elspec](http://www.elsevier.com/locate/elspec)



### Determination of the cation site distribution of the spinel in multiferroic $\text{CoFe}_2\text{O}_4/\text{BaTiO}_3$ layers by X-ray photoelectron spectroscopy



T. Aghavnian<sup>a,b</sup>, J.-B. Moussy<sup>a</sup>, D. Stanesco<sup>a</sup>, R. Belkhou<sup>b</sup>, N. Jedrecy<sup>c</sup>, H. Magnan<sup>a</sup>, P. Ohresser<sup>b</sup>, M.-A. Arrio<sup>d</sup>, Ph. Saintavrit<sup>d</sup>, A. Barbier<sup>a,\*</sup>

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<sup>b</sup> Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, F-91192 Gif-sur-Yvette, France

<sup>c</sup> Sorbonne Universités, UPMC Univ Paris 06, UMR 7588, INSP, F-75005 Paris, France

<sup>d</sup> IMPMC, F-75015 Paris, France

confirmation XMCD

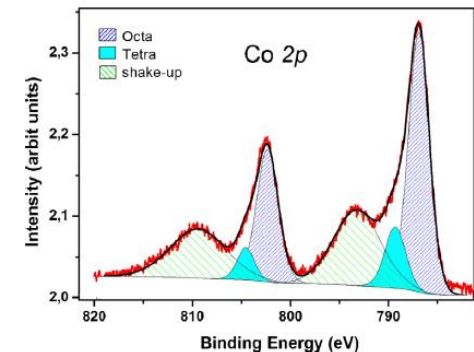
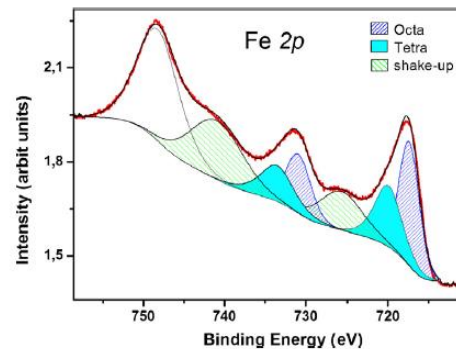


Fig. 5. XPS spectrum of Fe in  $\text{CoFe}_2\text{O}_4$  – decomposition in individual contribution: Fig. 4. XPS spectrum of Co in  $\text{CoFe}_2\text{O}_4$ , with the best fit peaks for sample 3.



Cite this: *J. Mater. Chem. C*, 2015,  
3, 6012

### p-Type conducting transparent characteristics of delafossite Mg-doped $\text{CuCrO}_2$ thin films prepared by RF-sputtering

A. Barnabé,\* Y. Thimont, M. Lalanne, L. Presmanes and P. Tailhades

The growth of technologically relevant compounds, Mg-doped  $\text{CuCrO}_2$  delafossite thin films, on a quartz substrate by radio-frequency sputtering is reported in this work. The deposition, performed at room temperature, leads to a nanocrystalline phase with extrinsic delafossite characteristic diffraction peaks were obtained as a function of the primary vacuum. The electrical conductivity was optimized until 1.63  $\times 10^{-3}$   $\Omega^{-1}\text{cm}^{-1}$  of 63% in the visible range by a 600 °C annealing treatment under vacuum. The transport properties were analyzed by Seebeck and Hall measurements and optical simulation. These measurements highlighted a degenerate hopping mechanism with a high hole concentration ( $10^{21}\text{ cm}^{-3}$ ). The direct optical bandgap of 3.3 eV has been measured and confirmed by two independent modellings of the optical transmittance. A p-type TCO optoelectronic characteristics have led to the highest performance reported so far for such delafossite materials.

Received 16th April 2015,  
Accepted 5th May 2015

DOI: 10.1039/c5tc01070e

www.rsc.org/MaterialsC

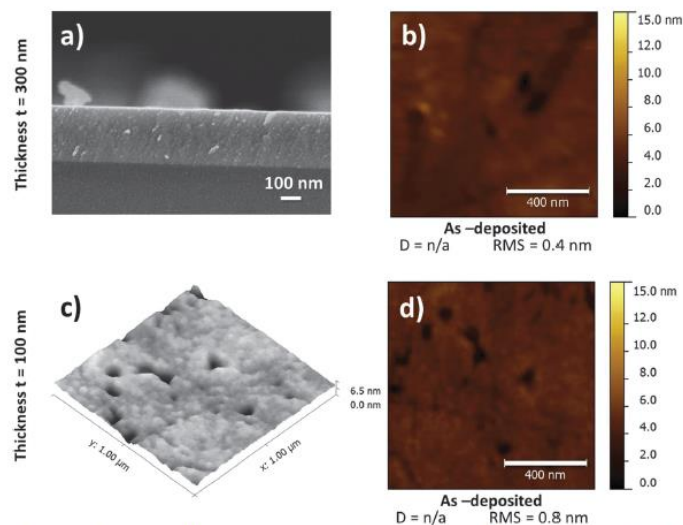


Fig. 3 (a) Cross section SEM and (b) surface AFM micrographs of 300 nm thick as-deposited thin film. The corresponding (c) 3D and (d) surface AFM micrographs of a 100 nm thick as-deposited film.

# Optoélectronique

Défi :  $\text{LiNbO}_3$  en films d'aussi bonne qualité que massif

Materials Chemistry and Physics 149-150 (2015) 622–631

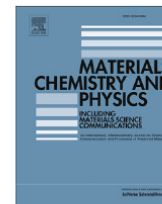


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Materials Chemistry and Physics

journal homepage: [www.elsevier.com/locate/matchemphys](http://www.elsevier.com/locate/matchemphys)



## Thickness dependent stresses and thermal expansion of epitaxial $\text{LiNbO}_3$ thin films on C-sapphire



A. Bartasyte <sup>a, b, \*</sup>, V. Plausinaitiene <sup>c</sup>, A. Abrutis <sup>c</sup>, S. Stanionyte <sup>c</sup>, S. Margueron <sup>d</sup>,  
V. Kubilius <sup>c</sup>, P. Boulet <sup>b</sup>, S. Huband <sup>e</sup>, P.A. Thomas <sup>e</sup>

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<sup>e</sup> *Department of Physics, University of Warwick, Coventry, UK*

# Composés X-chrome (thermochrome, électrochrome, photochrome...)

modulation des propriétés optiques par la température

JOURNAL OF APPLIED PHYSICS **111**, 113517 (2012)

## Thermochromic effect at room temperature of $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ thin films

A. Boileau,<sup>1</sup> F. Capon,<sup>1,a)</sup> S. Barrat,<sup>1</sup> P. Laffez,<sup>2</sup> and J. F. Pierson<sup>1</sup>

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<sup>2</sup>*Groupe de Recherche Electronique, Matériaux, Acoustique, Nanoscience (GREMAN), Université François Rabelais de Tours, UMR CNRS 7347, IUT de Blois, 15 rue de la Chocolaterie, Blois, F-41000, France*

(Received 24 April 2012; accepted 25 April 2012; published online 6 June 2012)

$\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  thermochromic thin films were synthesized using dc reactive magnetron co-sputtering and subsequent annealing in air. The film structure was studied by x-ray diffraction analysis. To validate the thermochromic potentiality of  $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ , electrical resistivity and infrared transmittance spectra were recorded for temperatures ranging from 77 K to 420 K. The temperature dependence of the optical band gap was estimated in the near infrared range. Upon heating, the optical transmission decreases in the infrared domain showing a thermochromic effect over a wide wavelength range at room temperature. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4722264>]

furtivité IR



# Ferroélectriques

aspects applicatifs - intégration électronique semi conducteurs

APPLIED PHYSICS LETTERS **103**, 212901 (2013)



## Ferroelectric Pb(Zr,Ti)O<sub>3</sub> epitaxial layers on GaAs

L. Louahadj,<sup>1</sup> D. Le Bourdais,<sup>2</sup> L. Largeau,<sup>3</sup> G. Agnus,<sup>2</sup> L. Mazet,<sup>4</sup> R. Bachelet,<sup>4</sup> P. Regreny,<sup>4</sup> D. Albertini,<sup>5</sup> V. Pillard,<sup>2</sup> C. Dubourdieu,<sup>4</sup> B. Gautier,<sup>4</sup> P. Lecoeur,<sup>2</sup> and G. Saint-Girons<sup>4,a)</sup>

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<sup>4</sup>Université de Lyon, Ecole Centrale de Lyon, INL-UMR5270-CNRS, 36 av. Guy de Collongue, F69134 Ecully Cedex, France

<sup>5</sup>Université de Lyon, INSA de Lyon, INL-UMR5270-CNRS, 20, avenue Albert Einstein, 69621 Villeurbanne, France

(Received 18 June 2013; accepted 31 October 2013; published online 18 November 2013)

Ferroelectric epitaxial Pb(Zr,Ti)O<sub>3</sub> (PZT) layers were grown by pulsed laser deposition on SrTiO<sub>3</sub>/GaAs templates fabricated by molecular beam epitaxy. The templates present an excellent structural quality and the SrTiO<sub>3</sub>/GaAs is abrupt at the atomic scale. The PZT layers contain a- and c-domains, as shown by X-Ray diffraction analyses. Piezoforce microscopy experiments and macroscopic electrical characterizations indicate that PZT is ferroelectric. A relative dielectric permittivity of 164 is extracted from these measurements. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4831738>]

# Ferroélectriques

« Strain engineering » dans des super réseaux

## Polarization Rotation in Ferroelectric Tricolor $\text{PbTiO}_3/\text{SrTiO}_3/\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ Superlattices

Nathalie Lemée,<sup>\*,§</sup> Ingrid C. Infante,<sup>#</sup> Cécile Hubault,<sup>§,†</sup> Alexandre Boule,<sup>‡</sup> Nils Blanc,<sup>⊥,||</sup>  
Nathalie Boudet,<sup>⊥,||</sup> Valérie Demange,<sup>¶</sup> and Michael G. Karkut<sup>§</sup>

<sup>§</sup>Laboratoire de Physique de la Matière Condensée, EA 2081, Université de Picardie Jules Verne, 80039 Amiens, France

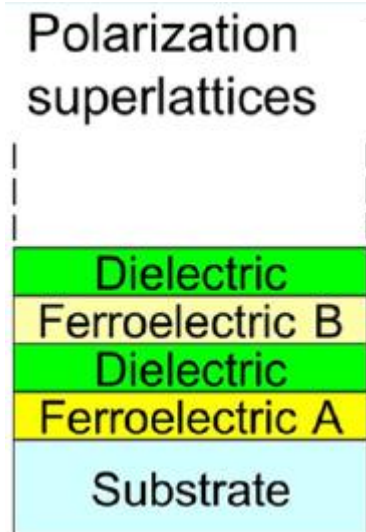
<sup>#</sup>Laboratoire Structures, Propriétés et Modélisation des Solides, CentraleSupélec, CNRS-UMR 8580, Université Paris-Saclay, 92295 Cedex Châtenay-Malabry, France

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*ACS Appl. Mater. Interfaces* 2015, 7, 19906–19913

degrés de liberté supplémentaires permis par les superréseaux  
réseaux bicolores, tricolores, le « strain engineering »  
stabilisation de la structure monoclinique  
intérêt pour les propriétés piézoélectriques

# Ferroélectriques

« Strain engineering » dans des super réseaux

APPLIED PHYSICS LETTERS **107**, 042904 (2015)



## Insight on the ferroelectric properties in a $(\text{BiFeO}_3)_2(\text{SrTiO}_3)_4$ superlattice from experiment and *ab initio* calculations

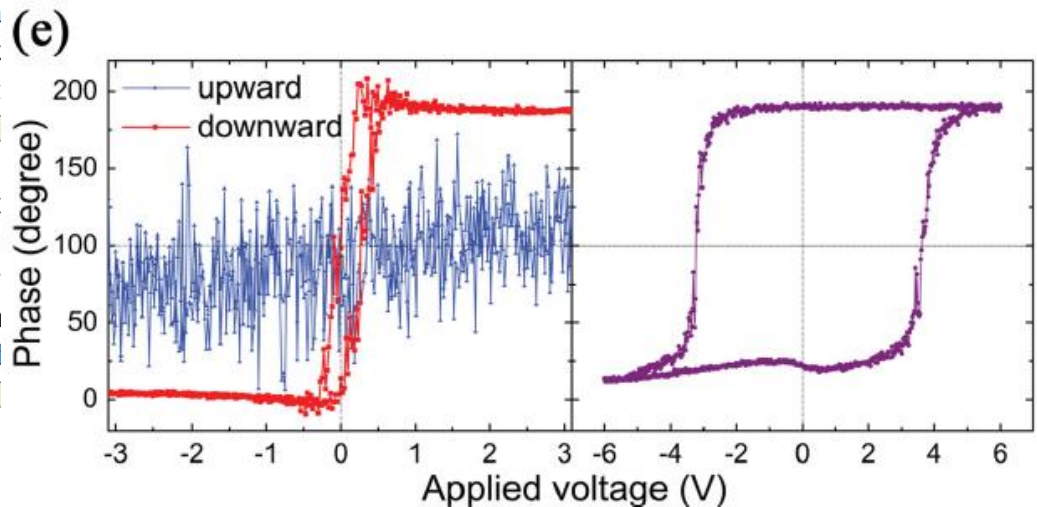
E. Bruyer,<sup>1,a)</sup> A. Sayede,<sup>1,a)</sup> A. Ferri,<sup>1</sup> R. Desfeux,<sup>1</sup> R. V. K. Mangalam,<sup>2,b)</sup> R. Ranjith,<sup>2,c)</sup> and W. Prellier<sup>2</sup>

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(Received 21 April 2015; accepted 18 July 2015; published online 28 July 2015)

Ferroelectric domain properties of a piezoresponse force microscopy and out-of-plane and in-plane piezorespo oriented along the out-of-plane [001] evidence that this orientation is due inside the superlattice in response to tions of the  $\text{BO}_2$  planes within both are highlighted. Besides, a much low  $\text{BiFeO}_3$  single layers, suggesting a m enable the design of promising multif [\[http://dx.doi.org/10.1063/1.4927600\]](http://dx.doi.org/10.1063/1.4927600)



T-like BFO en raison des contraintes interfaciales  
domaines ferroélectriques hors du plan  
modification du champ coercitif

# Ferroélectriques – Conscience environnementale

## Lead-Free $\alpha$ -La<sub>2</sub>WO<sub>6</sub> Ferroelectric Thin Films

Thomas Carlier,<sup>†</sup> Marie-Hélène Chambrier,<sup>\*,†</sup> Anthony Ferri,<sup>†</sup> Sonia Estradé,<sup>§</sup> Jean-François Blach,<sup>†</sup> Gemma Martín,<sup>§</sup> Belkacem Meziane,<sup>†</sup> Francesca Peiró,<sup>§</sup> Pascal Roussel,<sup>‡</sup> Freddy Ponchel,<sup>||</sup> Denis Rèmes,<sup>||</sup> Albert Cornet,<sup>§</sup> and Rachel Desfeux<sup>†</sup>

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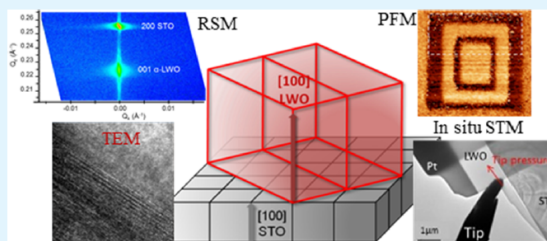
<sup>‡</sup>Unité de Catalyse et de Chimie du Solide, UMR 8181 CNRS, Ecole Nationale Supérieure Chimie Lille, Cité Scientifique, Bât C7, F-59652 Villeneuve d'Ascq, France

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<sup>||</sup>Institut d'Electronique, de Microélectronique et de Nanotechnologies, DOAE, UMR 8520 CNRS, Université de Valenciennes et du Hainaut-Cambrésis, F-59313 Valenciennes 9, France

**ABSTRACT:** (001)-Epitaxial La<sub>2</sub>WO<sub>6</sub> (LWO) thin films are grown by pulsed laser deposition on (001)-oriented SrTiO<sub>3</sub> (STO) substrates. The  $\alpha$ -phase (high-temperature phase in bulk) is successfully stabilized with an orthorhombic structure ( $a = 16.585(1) \text{ \AA}$ ,  $b = 5.717(2) \text{ \AA}$ ,  $c = 8.865(5) \text{ \AA}$ ). X-ray-diffraction pole-figure measurements suggest that crystallographic relationships between the film and substrate are  $[100]_{\text{LWO}} \parallel [110]_{\text{STO}}$ ,  $[010]_{\text{LWO}} \parallel [1\bar{1}0]_{\text{STO}}$  and  $[001]_{\text{LWO}} \parallel [001]_{\text{STO}}$ . From optical properties, investigated by spectroscopic ellipsometry, we extract a refractive-index value around 2 (at 500 nm) along with the presence of two absorption bands situated, respectively at 3.07 and 6.32 eV. Ferroelectricity is evidenced as well on macroscale (standard polarization measurements) as on nanoscale, calling for experiments based on piezo-response force-microscopy, and confirmed with in situ scanning-and-tunneling measurements performed with a transmission electron microscope. This work highlights the ferroelectric behavior, at room temperature, in high-temperature LWO phase when stabilized in thin film and opens the way to new functional oxide thin films dedicated to advanced electronic devices.

**KEYWORDS:** pulsed laser deposition, high-resolution X-ray diffraction, transmission electron microscopy, ferroelectricity, piezoresponse force microscopy



Propriétés  
piézoélectriques : sonars,  
frequency filters, gas  
ignitors, ultrasonic and  
medical diagnosis  
transducers, surveillance  
devices, and FeRAM  
memories

Matériaux connus en  
massif  
de piezoélectricité non  
vraiment étudiée  
de groupe d'espace non  
centrosymétrique  
d'où l'idée de les faire en  
couches minces

## Nanorods of Potassium Tantalum Niobate Tetragonal Tungsten Bronze Phase Grown by Pulsed Laser Deposition

Q. Simon,<sup>†,§</sup> V. Dorcet,<sup>†</sup> P. Boullay,<sup>‡</sup> V. Demange,<sup>\*,†</sup> S. Députier,<sup>†</sup> V. Bouquet,<sup>†</sup> and M. Guilloux-Viry<sup>†</sup>

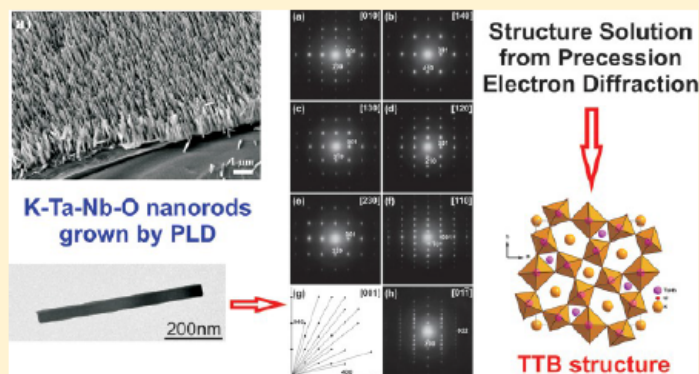
<sup>†</sup>Institut des Sciences Chimiques de Rennes, ISCR - UMR 6226 CNRS/Université de Rennes 1, 263, avenue du Général Leclerc, CS 74205, 35042 Rennes Cedex, France

<sup>‡</sup>Laboratoire de Cristallographie et Sciences des Matériaux, CRISMAT – UMR 6508 CNRS/ENSICAEN, 6, boulevard du Maréchal Juin, 14050 Caen Cedex 4, France

**S** Supporting Information

**ABSTRACT:** K–Ta–Nb–O tetragonal tungsten bronze phase was grown on (1 $\bar{1}$ 02) Al<sub>2</sub>O<sub>3</sub> (R-plane sapphire) by pulsed laser deposition. The microstructure, structure, and chemical composition of the deposit were studied by scanning electron microscopy, X-ray diffraction, energy-dispersive X-ray spectrometry, and transmission electron microscopy. The crystal structure was solved by precession electron diffraction as being tetragonal tungsten bronze-type structure with space group *P4/mbm*, refined cell parameters  $a = 12.537 \pm 0.003 \text{ \AA}$ ,  $c = 3.975 \pm 0.001 \text{ \AA}$ , and composition  $\text{K}_{5.06}(\text{Ta}_{0.57}\text{Nb}_{0.43})_{10.99}\text{O}_{30}$ . The tetragonal potassium tantalum niobate growth follows two modes with respect to the substrate surface: (i) as single vertical right parallelepiped-shaped nanorods (50 to 100 nm wide and up to 1  $\mu\text{m}$  in length) along the [001] direction and (ii) as in-plane attached crystals along the  $\langle 310 \rangle$  direction. These two growth modes are understood as being governed by the plane termination of the substrate. This new phase is of potential interest due to the physical (dielectric, catalytic, etc.) properties evidenced for tetragonal tungsten bronze phases in numerous systems.

**KEYWORDS:** KTN, TTB, PLD, TEM, crystal structure, precession electron diffraction





Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: [www.elsevier.com/locate/ssscie](http://www.elsevier.com/locate/ssscie)



## Dielectric properties of tetragonal tungsten bronze films deposited by RF magnetron sputtering

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*Ba<sub>2</sub>LnFeNb<sub>4</sub>O<sub>15</sub> thin films*

propriétés diélectriques des couches minces similaires au massif  
importance de la stoechiométrie en O (recuit sous O<sub>2</sub>)

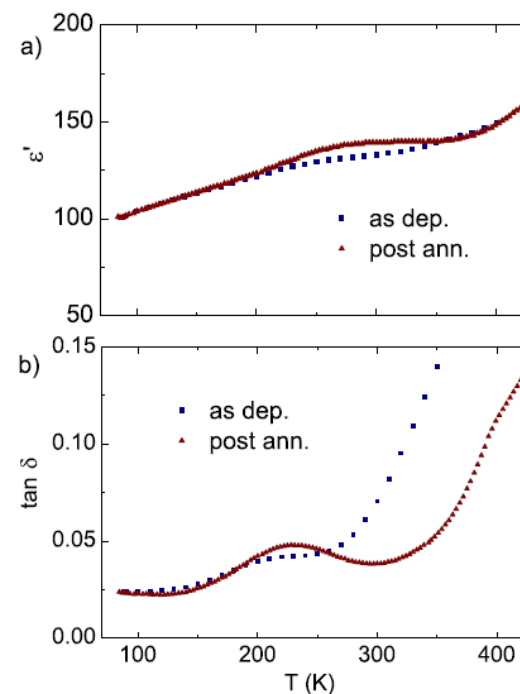


Fig. 8. Temperature dependence of the dielectric constant  $\epsilon'$  (a) and the dielectric loss  $\tan \delta$  (b) for both as-deposited and post annealed BNdFN films at 1 MHz.

# Ferroélectriques – Conscience environnementale

## Enhancement of piezoelectric response in Ga doped BiFeO<sub>3</sub> epitaxial thin films

N. Jaber,<sup>1</sup> J. Wolfman,<sup>1,a)</sup> C. Daumont,<sup>1</sup> B. Négulescu,<sup>1</sup> A. Ruyter,<sup>1</sup> G. Feuillard,<sup>1</sup>  
M. Bavencoffe,<sup>1</sup> J. Fortineau,<sup>1</sup> T. Sauvage,<sup>2</sup> B. Courtois,<sup>2</sup> H. Bouyanfif,<sup>3</sup> J. L. Longuet,<sup>4</sup>  
C. Autret-Lambert,<sup>1</sup> and F. Gervais<sup>1</sup>

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(Received 13 May 2015; accepted 17 June 2015; published online 30 June 2015)

The piezoelectric properties of compositional spread  $(1-x)\text{BiFeO}_3-x\text{GaFeO}_3$  epitaxial thin films are investigated where  $\text{Ga}^{3+}$  substitution for  $\text{Bi}^{3+}$  is attempted in  $\text{Bi}_{1-x}\text{Ga}_x\text{FeO}_3$  compounds. Ga content  $x$  was varied from 0 to 12% (atomic). Ferroelectric characterizations are reported at various length scales. Around 6.5% of Ga content, an enhancement of the effective piezoelectric coefficient  $d_{33}^{\text{eff}}$  is observed together with a change of symmetry of the film. Measured  $d_{33}^{\text{eff}}$  values in 135 nm thick films increased from 25 pm/V for undoped  $\text{BiFeO}_3$  to 55 pm/V for 6.5% Ga with no extrinsic contribution from ferroelastic domain rearrangement. © 2015 AIP Publishing LLC.

[<http://dx.doi.org/10.1063/1.4923217>]

zone morphotropique dans le système  
 $\text{GaFeO}_3\text{-BiFeO}_3$

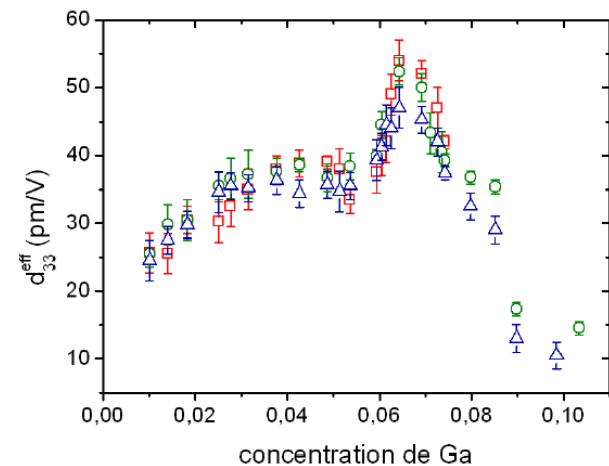


Figure 5.5.  $d_{33}^{\text{eff}}$  en fonction de la concentration en Ga pour trois séries d'électrodes.

# Ferroélectriques – Conscience environnementale

## Aspects applicatifs : résonateurs accordables

Thin Solid Films 553 (2014) 109–113



Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: [www.elsevier.com/locate/tsf](http://www.elsevier.com/locate/tsf)



### Study of ferroelectric/dielectric multilayers for tunable stub resonator applications at microwaves



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<sup>c</sup> Lab-STICC, UMR-CNRS 6285, Université de Bretagne Occidentale, 6 Avenue Le Gorgeu, 29238 Brest, France

#### ARTICLE INFO

Available online 20 November 2013

#### Keywords:

Dielectric/ferroelectric heterostructure  
Multilayer  
Dielectric film  
Ferroelectric film  
Tunable resonator  
Microwave

#### ABSTRACT

Tunable coplanar waveguide stub resonators deposited on various ferroelectric/dielectric heterostructures are studied in the 10-GHz band. A frequency tunability of up to ~45% is achieved under a moderate biasing field ( $E_{bias} < 100$  kV/cm) when the resonator is printed on  $KTa_{0.5}Nb_{0.5}O_3$  (KTN) ferroelectric thin film alone: this comes from the large permittivity agility of the KTN material ( $\epsilon_{r(KTN)}$  varies from ~700 to ~200). Nevertheless this also leads to significant insertion loss due to the dielectric loss of the ferroelectric material itself ( $\tan\delta_{r(KTN)} \approx 0.15$ –0.30 at 10 GHz). In this paper, an original route has been considered to reduce the device loss while keeping up a high frequency tunability. It consists in associating the KTN film with a dielectric film to elaborate ferroelectric/dielectric multilayers. The  $Bi_{1.5}Zn_{0.9}Nb_{1.5}O_{7-6}$  (BZN) oxide material is selected here for two main reasons, namely its low dielectric loss ( $\tan\delta_{r(BZN)} \approx 0.005$ –0.0075) and its moderate relative permittivity ( $\epsilon_{r(BZN)} \approx 95$ –125) at 12.5 GHz. The relevance of this approach is studied numerically and experimentally. We compare numerically two different heterostructures for which the ferroelectric film is grown on the dielectric film (KTN/BZN), or vice versa (BZN/KTN). A stub resonator printed on the most relevant heterostructure has been fabricated, and experimental data are discussed and compared to the numerical results.

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# Effets d'interfaces

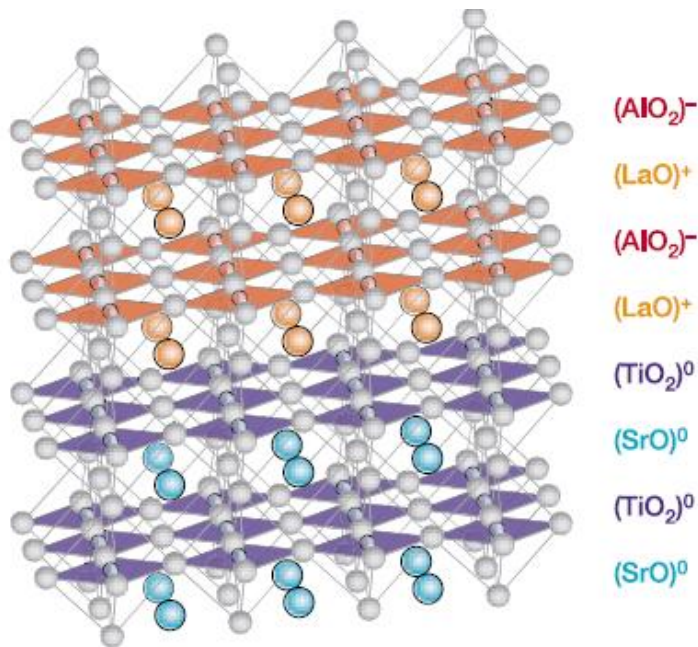
## A high-mobility electron gas at the $\text{LaAlO}_3/\text{SrTiO}_3$ heterointerface

A. Ohtomo<sup>1,2,3</sup> & H. Y. Hwang<sup>1,3,4</sup>

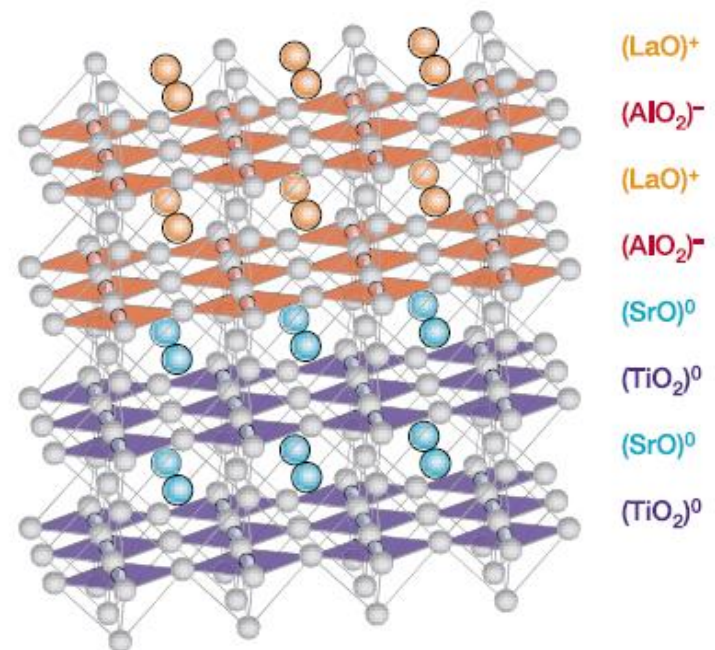
NATURE | VOL 427 | 29 JANUARY 2004 | [www.nature.com/nature](http://www.nature.com/nature)

$\text{LaAlO}_3$  : isolant large band gap 5.6 eV

$\text{SrTiO}_3$  : isolant large band gap 3.2 eV



$(\text{AlO}_2)^- / (\text{SrO})^0$  interface : isolante

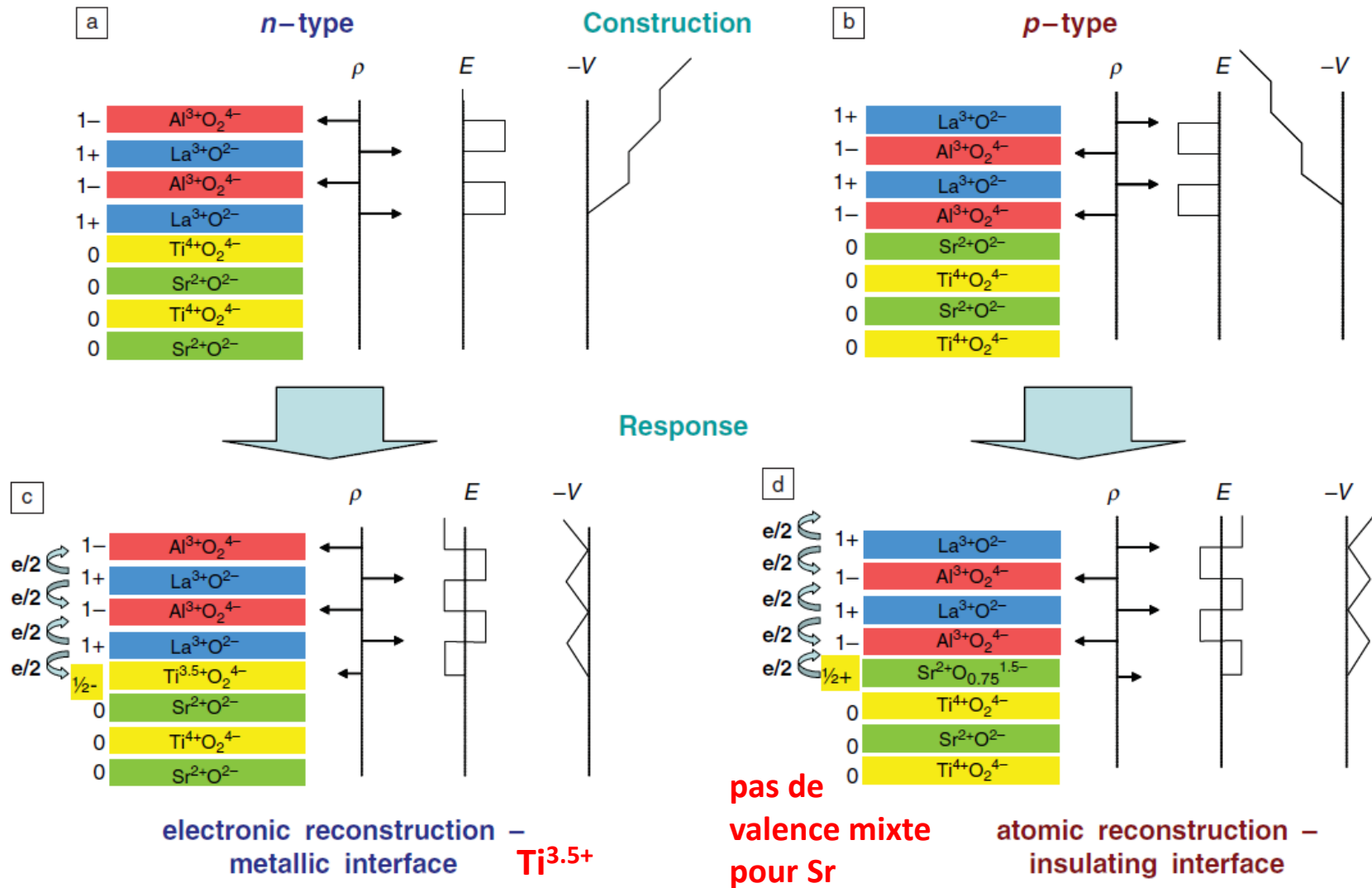


$(\text{LaO})^+ / (\text{TiO}_2)^0$  interface : conductrice

# Why some interfaces cannot be sharp

NAOYUKI NAKAGAWA<sup>1,2</sup>, HAROLD Y. HWANG<sup>1,2</sup> AND DAVID A. MULLER<sup>3\*</sup>

nature materials | VOL 5 | MARCH 2006 |



## Towards Two-Dimensional Metallic Behavior at $\text{LaAlO}_3/\text{SrTiO}_3$ Interfaces

O. Copie,<sup>1</sup> V. Garcia,<sup>1</sup> C. Bödefeld,<sup>2</sup> C. Carrétéro,<sup>1</sup> M. Bibes,<sup>1</sup> G. Herranz,<sup>1,\*</sup> E. Jacquet,<sup>1</sup> J.-L. Maurice,<sup>1</sup> B. Vinter,<sup>1,3</sup> S. Fusil,<sup>1,4</sup> K. Bouzouane,<sup>1</sup> H. Jaffrès,<sup>1</sup> and A. Barthélémy<sup>1,†</sup>

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<sup>2</sup>Attocube System AG, Königinstrasse 11a RGB, D-80539 München, Germany

<sup>3</sup>Physics Department, University of Nice-Sophia Antipolis, Parc Valrose, 06102 Nice Cedex 2, France

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(Received 13 February 2009; published 29 May 2009)

Using a low-temperature conductive-tip atomic force microscope in cross-section geometry we have characterized the local transport properties of the metallic electron gas that forms at the interface between  $\text{LaAlO}_3$  and  $\text{SrTiO}_3$ . At low temperature, we find that the carriers do not spread away from the interface but are confined within  $\sim 10$  nm, just like at room temperature. Simulations of the large temperature and electric-field dependence of the permittivity of  $\text{SrTiO}_3$  at a few nm for sheet carrier densities larger than  $\sim 6 \times 10^{13} \text{ cm}^{-2}$ . We find that our simulation results in terms of a multiband carrier system. Remarkably, the length scale from Hall measurements is  $\sim 16$  nm, indicating that the electron gas in or

DOI: 10.1103/PhysRevLett.102.216804

PACS numbers

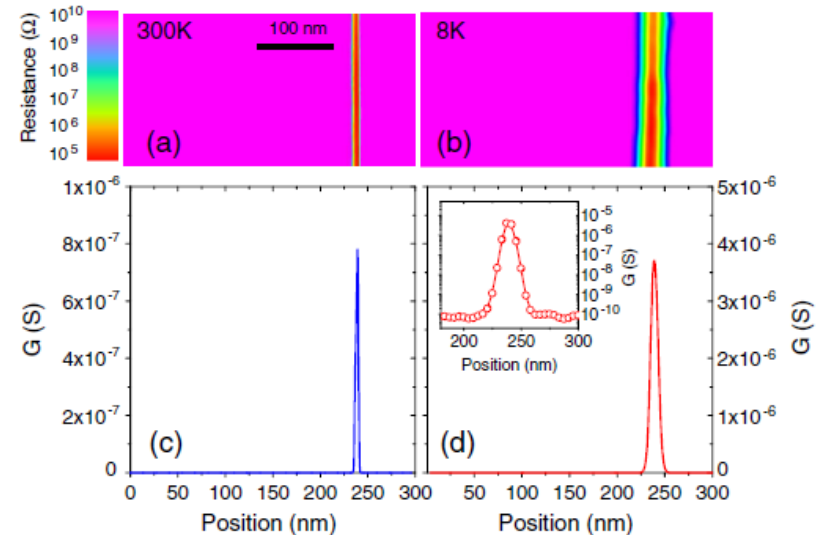
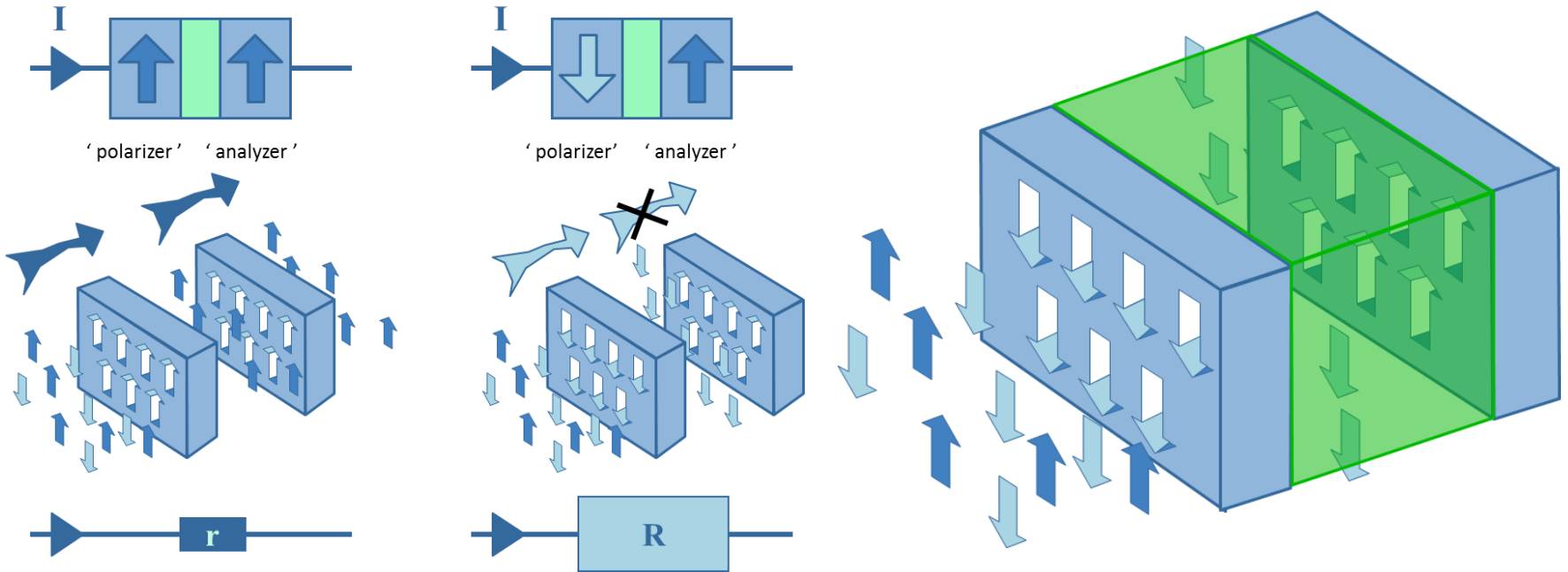


FIG. 1 (color online). CTAFM images in cross section geometry collected at 300 (a) and 8 K (b). Corresponding conductance profiles (c),(d). The inset in (d) shows the same data in logarithmic scale.

# Matériaux pour l'électronique de spin

métiers : injection de spin, propagation, manipulation, détection



Manipulation :  
nouveaux modes de contrôle  
basse consommation d'énergie

matériaux multifonctionnels  
matériaux multiferroïques

intrinsèques  
hétérostructures : exploitation des nombreuses  
interactions possibles

# Filtres de spin

APPLIED PHYSICS LETTERS **104**, 182404 (2014)



## Structure, magnetic ordering, and spin filtering efficiency of NiFe<sub>2</sub>O<sub>4</sub>(111) ultrathin films

S. Matzen,<sup>1,a)</sup> J.-B. Moussy,<sup>1,b)</sup> P. Wei,<sup>2</sup> C. Gatel,<sup>3</sup> J. C. Cezar,<sup>4,c)</sup> M. A. Arrio,<sup>5</sup>  
Ph. Saintavit,<sup>5</sup> and J. S. Moodera<sup>2,6</sup>

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<sup>2</sup>Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

<sup>3</sup>CEMES-CNRS, F-31055 Toulouse, France

<sup>4</sup>ESRF, F-38043 Grenoble, France

<sup>5</sup>IMPIC, F-75015 Paris, France

<sup>6</sup>Physics Department, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

(Received 20 November 2013; accepted 7 April 2014; published online 6 May 2014)

NiFe<sub>2</sub>O<sub>4</sub>(111) ultrathin films (3–5 nm) have been grown by oxygen-assisted molecular beam epitaxy and integrated as effective spin-filter barriers. Structural and magnetic characterizations have been performed in order to investigate the presence of defects that could limit the spin filtering efficiency. These analyses have revealed the full strain relaxation of the layers with a cationic order in agreement with the inverse spinel structure but also the presence of antiphase boundaries. A spin-polarization up to +25% has been directly measured by the Meservey-Tedrow technique in Pt(111)/NiFe<sub>2</sub>O<sub>4</sub>(111)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(111)/Al tunnel junctions. The unexpected positive sign and relatively small value of the spin-polarization are discussed, in comparison with predictions and previous indirect tunnelling magnetoresistance measurements. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4871733>]

## Towards electrical spin injection into $\text{LaAlO}_3\text{--SrTiO}_3$

BY M. BIBES\*, N. REYREN, E. LESNE, J.-M. GEORGE, C. DERANLOT,  
S. COLLIN, A. BARTHÉLÉMY AND H. JAFFRÈS

*Unité Mixte de Physique CNRS-Thales, 1 Avenue Augustin Fresnel,  
91767 Palaiseau, France and Université Paris-Sud, 91405 Orsay, France*

Future spintronics devices will be built from elemental blocks allowing the electrical injection, propagation, manipulation and detection of spin-based information. Owing to their remarkable multi-functional and strongly correlated character, oxide materials already provide such building blocks for charge-based devices such as ferroelectric field-effect transistors (FETs), as well as for spin-based two-terminal devices such as magnetic tunnel junctions, with giant responses in both cases. Until now, the lack of suitable channel materials and the uncertainty of spin-injection conditions in these compounds had however prevented the exploration of similar giant responses in oxide-based lateral spin transport structures. In this paper, we discuss the potential of oxide-based spin FETs and report magnetotransport data that suggest electrical spin injection into the  $\text{LaAlO}_3\text{--SrTiO}_3$  interface system. In a local, three-terminal measurement scheme, we analyse the voltage variation associated with the precession of the injected spin accumulation driven by perpendicular or longitudinal magnetic fields (Hanle and ‘inverted’ Hanle effects). The spin accumulation signal appears to be much larger than expected, probably owing to amplification effects by resonant tunnelling through localized states in the  $\text{LaAlO}_3$ . We give perspectives on how to achieve direct spin injection with increased detection efficiency, as well on the implementation of efficient top gating schemes for spin manipulation.

**Keywords:** oxide interfaces; spin injection; spintronics

# Transport dépendant en spin

## Magnétisme basse dimensionalité

APPLIED PHYSICS LETTERS **102**, 212407 (2013)



### Epitaxial growth of $\gamma$ -CoV<sub>2</sub>O<sub>6</sub> thin films: Structure, morphology, and magnetic properties

M. Lenertz, S. Colis,<sup>a)</sup> C. Ulhaq-Bouillet, and A. Dinia

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(Received 25 March 2013; accepted 3 May 2013; published online 29 May 2013)

We report on the epitaxial growth of 100 nm thick triclinic  $\gamma$ -CoV<sub>2</sub>O<sub>6</sub> thin films deposited by pulsed laser deposition on TiO<sub>2</sub>(100) substrate. The layers were grown in narrow experimental conditions, at 600 °C and 0.1 millibar oxygen pressure. X-ray diffraction and transmission electron microscopy evidenced the presence of two variants and the following epitaxial relation between the layers and the substrate: [001]TiO<sub>2</sub>(100) || [0±10] $\gamma$ -CoV<sub>2</sub>O<sub>6</sub>(100). Besides the magnetization steps expected in  $\gamma$ -CoV<sub>2</sub>O<sub>6</sub>, low temperature magnetic measurements performed along different crystalline axes show the existence of a strong anisotropy compatible with that expected from a one dimensional system, with the easy magnetization axis lying along the *b* direction (i.e., the Co chains). © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4808205>]

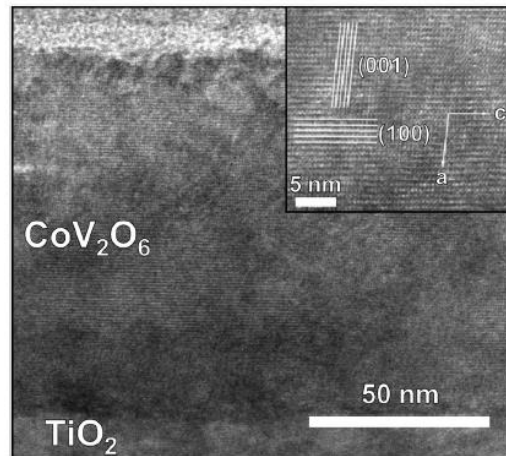


FIG. 4. Cross section bright field TEM image of a 100 nm thick  $\gamma$ -CoV<sub>2</sub>O<sub>6</sub> film: low magnification (main image) and high resolution (inset). The high resolution image was recorded along the [001]TiO<sub>2</sub> azimuth.

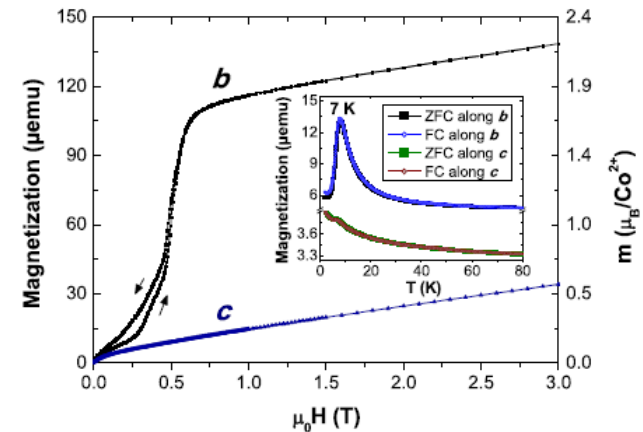


FIG. 6. Magnetization curve at 1.8 K of  $\gamma$ -CoV<sub>2</sub>O<sub>6</sub> recorded along the *b* (black) and *c* (blue) directions. The inset shows the field cooling and zero field cooling variation of the magnetization with temperature under 0.1 T constant magnetic field.

# Modulation anisotropie

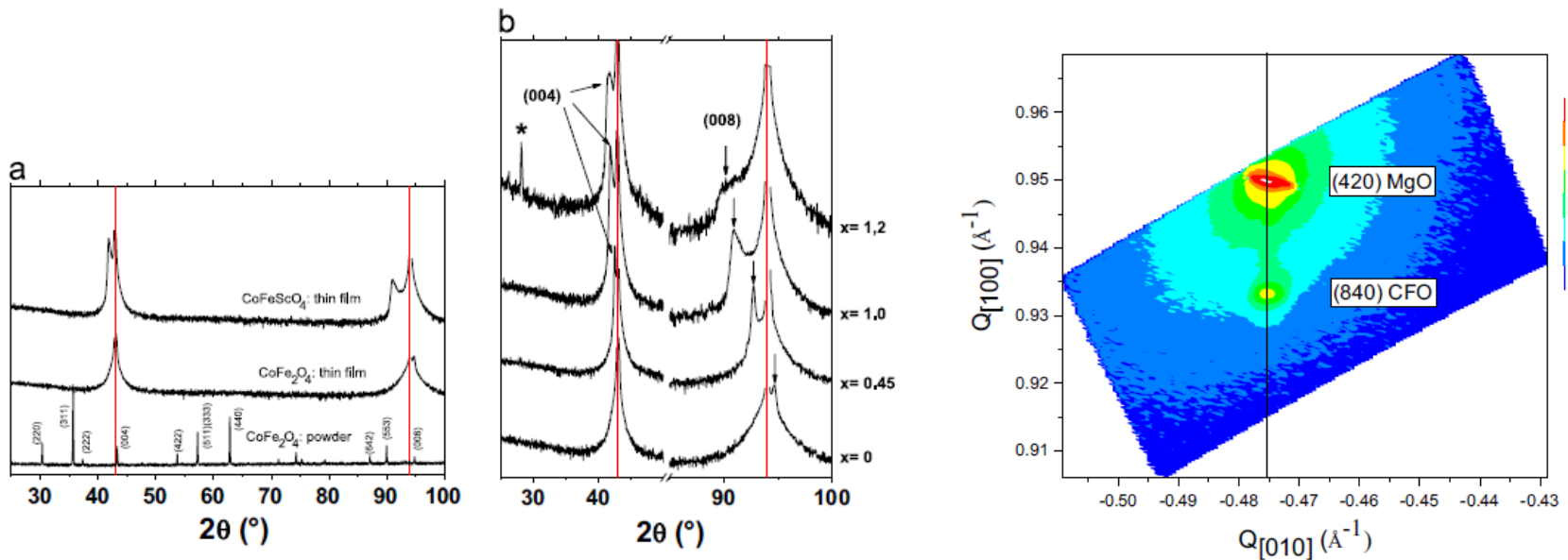
Dopages importants, non réalisables en massif

## Stabilization of scandium rich spinel ferrite $\text{CoFe}_{2-x}\text{Sc}_x\text{O}_4$ ( $x \leq 1$ ) in thin films

Christophe Lefevre\*, François Roulland, Alexandre Thomasson, Emmanuel Autissier, Cédric Leuvrey, Sophie Barre, Gilles Versini, Nathalie Viart, Geneviève Pourroy

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Journal of Solid State Chemistry 232 (2015) 118–122





# Manipulation

## Contrôle optique de l'aimantation

PHYSICAL REVIEW B 91, 184415 (2015)

### Excitation of magnetic precession in bismuth iron garnet via a polarization-independent impulsive photomagnetic effect

Benny Koene,<sup>1,\*</sup> Marwan Deb,<sup>2</sup> Elena Popova,<sup>2</sup> Niels Keller,<sup>2</sup> Theo Rasing,<sup>1</sup> and Andrei Kirilyuk<sup>1</sup>

<sup>1</sup>Radboud University Nijmegen, Institute for Molecules and Materials, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

<sup>2</sup>GEMaC, CNRS-Université de Versailles St. Quentin en Yvelines, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France

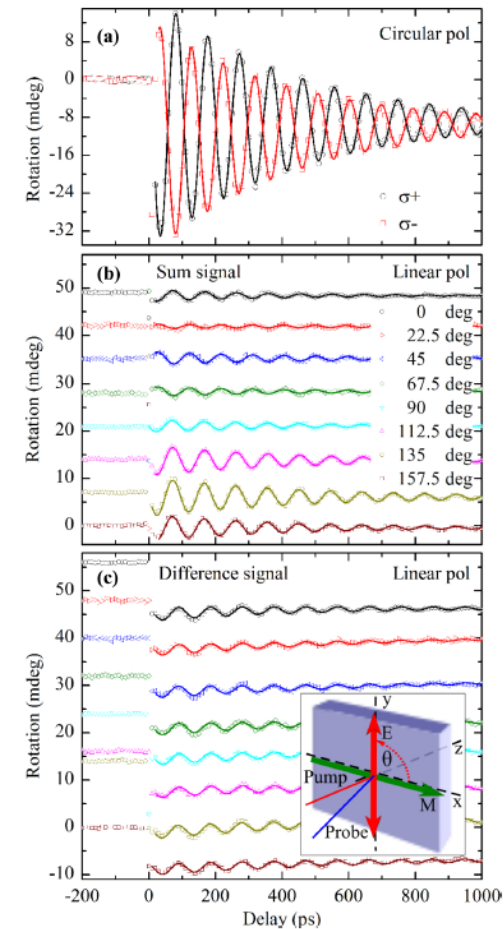
(Received 4 November 2014; revised manuscript received 5 May 2015; published 26 May 2015)

A polarization-independent, nonthermal optical effect on the magnetization in bismuth iron garnet is found, in addition to the circular polarization-dependent inverse Faraday effect and the linear polarization-dependent photoinduced magnetic anisotropy. Its impulsive character is demonstrated by the field dependence of the amplitude of the resulting precession, which cannot be explained by a long-living photo or heat-induced anisotropy.

Contrôle de la dynamique d'aimantation par des pulses laser femtoseconde

Possibilité de contrôle optique de l'aimantation

Matériau : BIG – large constante magnéto-optique

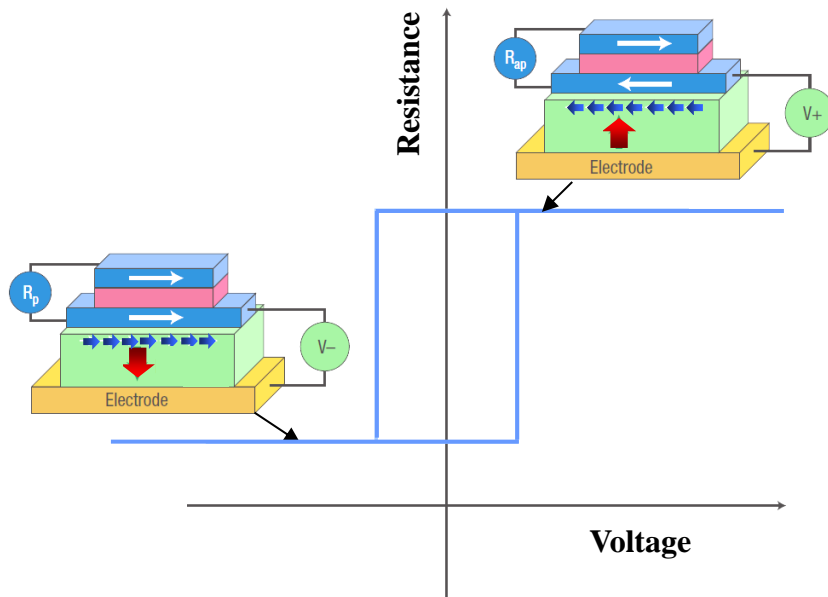


# Contrôle électrique de l'aimantation

concept

## Towards a magnetoelectric memory

M. Bibes et al., Nature Materials 7 (6), 425 (2008)

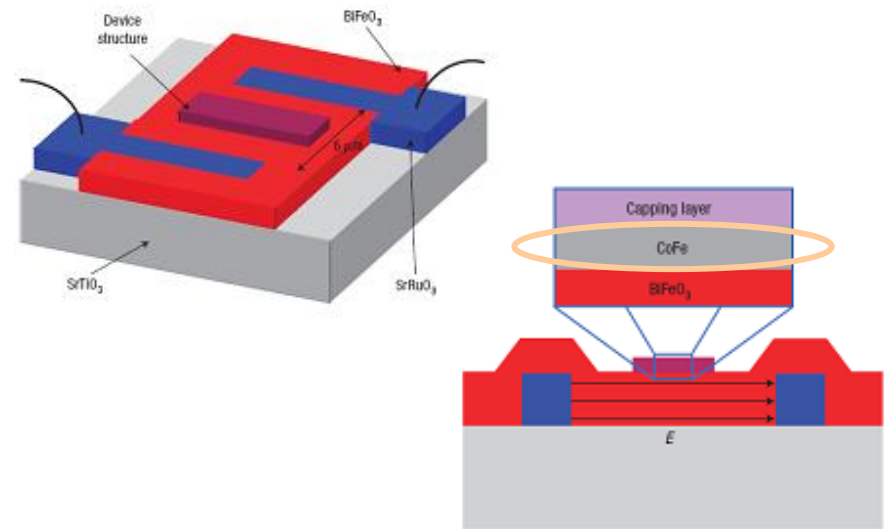


Mémoires magnétoélectriques combinent les avantages des M-RAM et Fe-RAM

preuve de concept

Electric-field control of local ferromagnetism using a magnetoelectric multiferroic

Y. H. Chu et al., Nature Materials 7 (8), 678 (2008)



**BiFeO<sub>3</sub>**  
Antiferromagnétique / ferroélectrique  
à température ambiante

# Contrôle électrique de l'aimantation – les multiferroïques

## BiFeO<sub>3</sub> : un matériau riche en possibilités

### Topical Review

## BiFeO<sub>3</sub> epitaxial thin films and devices: past, present and future

D Sando<sup>1,2</sup>, A Barthélémy<sup>1</sup> and M Bibes<sup>1</sup>

<sup>1</sup> Unité Mixte de Physique CNRS/Thales, 1 Avenue Fresnel, Campus de l'Ecole Polytechnique, 91767 Palaiseau, France, and Université Paris Sud, 91405 Orsay, France

<sup>2</sup> Center for Correlated Electron Systems, Institute for Basic Science (IBS), and Department of Physics and Astronomy, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 151-747, Republic of Korea

E-mail: [sandodm@gmail.com](mailto:sandodm@gmail.com) and [manuel.bibes@thalesgroup.com](mailto:manuel.bibes@thalesgroup.com)

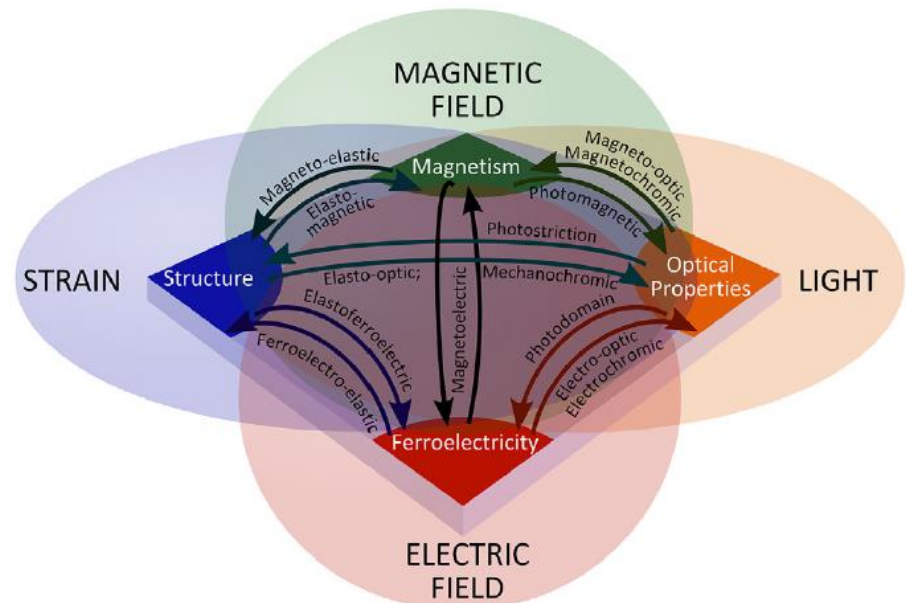
Received 5 May 2014, revised 11 September 2014

Accepted for publication 12 September 2014

Published 29 October 2014

### Abstract

The celebrated renaissance of the multiferroics family over the past ten years has also been that of its most paradigmatic member, bismuth ferrite (BiFeO<sub>3</sub>). Known since the 1960s as a high temperature antiferromagnet and since the 1970s to be ferroelectric, BiFeO<sub>3</sub> only had its bulk ferroic properties clarified in the mid-2000s. It is however the fabrication of BiFeO<sub>3</sub> thin films and their integration into epitaxial oxide heterostructures that have fully revealed an extraordinarily broad palette of functionalities. Here we review the first decade of research on BiFeO<sub>3</sub> films, restricting ourselves to epitaxial structures. We discuss how thickness and epitaxial strain influence not only the unit cell parameters, but also the crystal structure, illustrated for instance by the discovery of the so-called T-like phase of BiFeO<sub>3</sub>. We then present its ferroelectric and piezoelectric properties and their evolution near morphotropy phase boundaries. Magnetic properties and their modification by thickness and strain, as well as optical parameters, are covered. Finally, we highlight various types of device on BiFeO<sub>3</sub> in electronics, spintronics, and optics, and provide perspectives for the development of further multifunctional devices for information technology and energy harvesting.



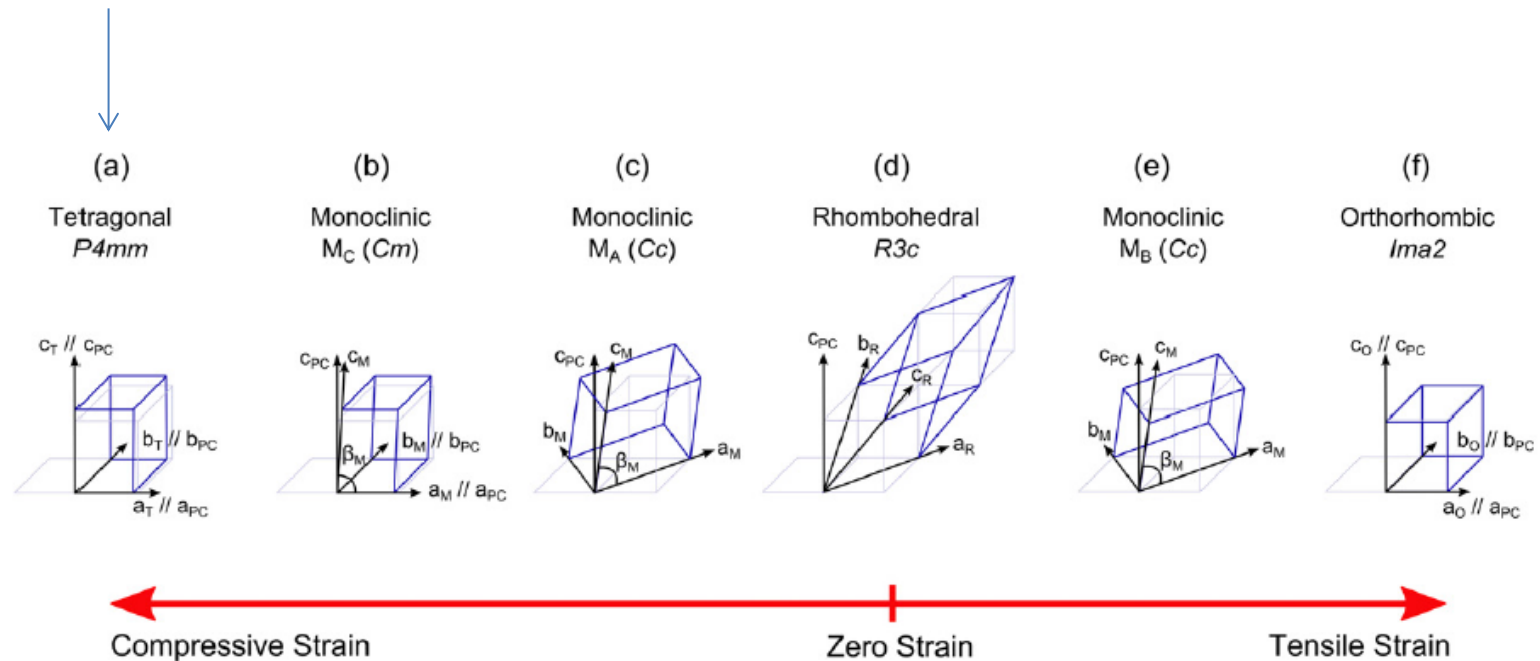
# Influence du substrat

Topical Review

## BiFeO<sub>3</sub> epitaxial thin films and devices: past, present and future

D Sando<sup>1,2</sup>, A Barthélémy<sup>1</sup> and M Bibes<sup>1</sup>

n'existe pas dans le bulk



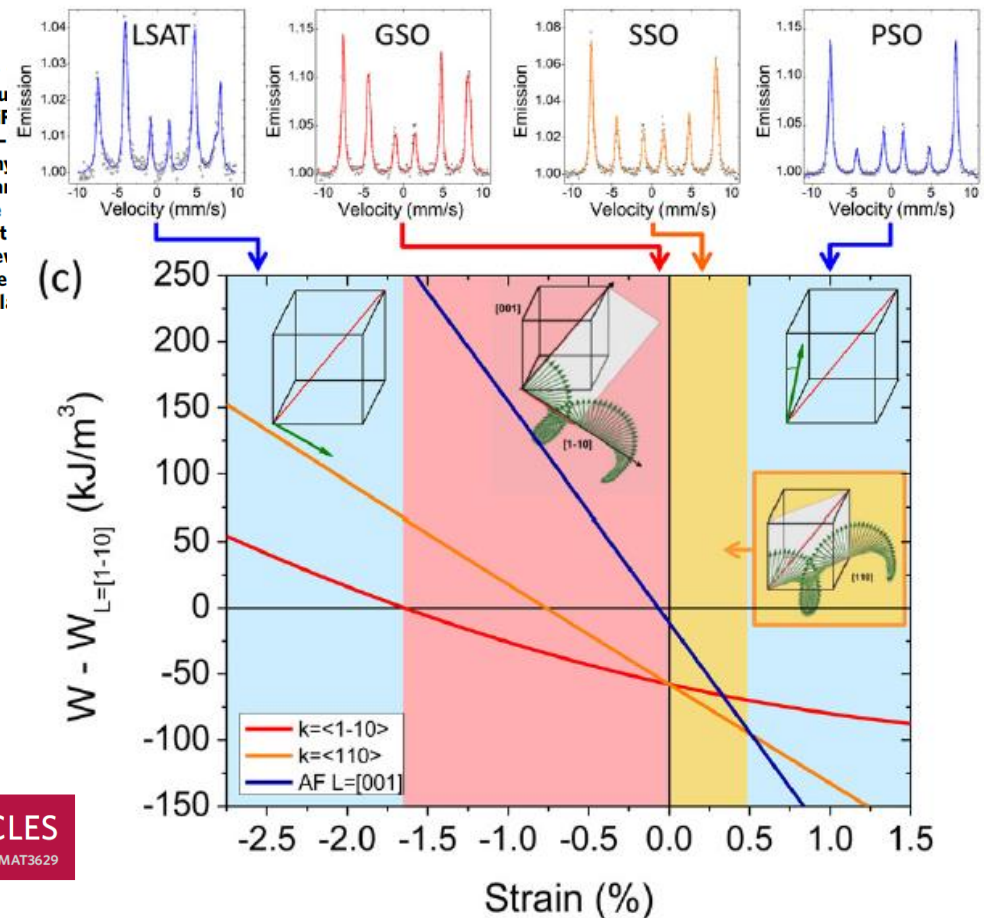
**Figure 3.** Summary of the various crystal structures that BFO forms in thin films. (a) Tetragonal BFO, only for very thin films; (b) the highly-distorted T-like monoclinic  $Cm$  phase, for strong compressive strain; (c) the  $M_A$  monoclinic phase, for moderate compressive strain; (d) the bulk-like rhombohedral phase that forms on (1 1 1)-oriented substrates; (e) the  $M_B$  monoclinic phase that forms at moderate tensile strain; and (f) the orthorhombic phase that can be stabilized by moderate tensile strain. The unit cells are shown relative to the primitive pseudocubic perovskite unit cell (light grey).

# Influence du substrat

## Crafting the magnonic and spintronic response of BiFeO<sub>3</sub> films by epitaxial strain

D. Sando<sup>1</sup>, A. Agbelele<sup>2</sup>, D. Rahmedov<sup>3</sup>, J. Liu<sup>4</sup>, P. Rovillain<sup>4†</sup>, C. Toulouse<sup>4</sup>, I. C. Infante<sup>1,5</sup>, A. P. Pyatakov<sup>6,7</sup>, S. Fusil<sup>1</sup>, E. Jacquet<sup>1</sup>, C. Carrétéro<sup>1</sup>, C. Deranlot<sup>1</sup>, S. Lisenkov<sup>8</sup>, D. Wang<sup>9</sup>, J.-M. Le Breton<sup>2</sup>, M. Cazayous<sup>4</sup>, A. Sacuto<sup>4</sup>, J. Juraszek<sup>2</sup>, A. K. Zvezdin<sup>6,10</sup>, L. Bellaiche<sup>3</sup>, B. Dkhil<sup>5</sup>, A. Barthélémy<sup>1</sup> and M. Bibes<sup>1\*</sup>

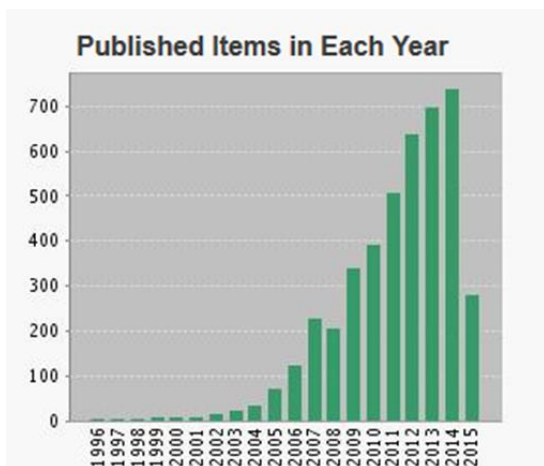
Multiferroics are compounds that show ferroelectricity and magnetism. BiFeO<sub>3</sub>, by far ferroelectric properties, a cycloidal magnetic order in the bulk, and many unexpected virtues or a low bandgap of interest for photovoltaics. Although this flurry of properties makes BiFeO<sub>3</sub> a multifunctional material, most are related to its ferroelectric character, and its other ferroic property—investigated extensively, especially in thin films. Here we bring insight into the rich spin physics of the static and dynamic magnetic response of strain-engineered films. Using Mössbauer spectroscopy with Landau-Ginzburg theory and effective Hamiltonian calculations, we show that the magnetic order that exists at low compressive strain is driven towards pseudo-collinear antiferromagnetism. For moderate tensile strain we also predict and observe indications of a new magnetic phase where the magnonic response is entirely modified, with low-energy magnon modes being suppressed. Our results reveal that strain progressively drives the average spin angle from in-plane to out-of-plane, and the exchange bias and giant-magnetoresistive response of spin valves.



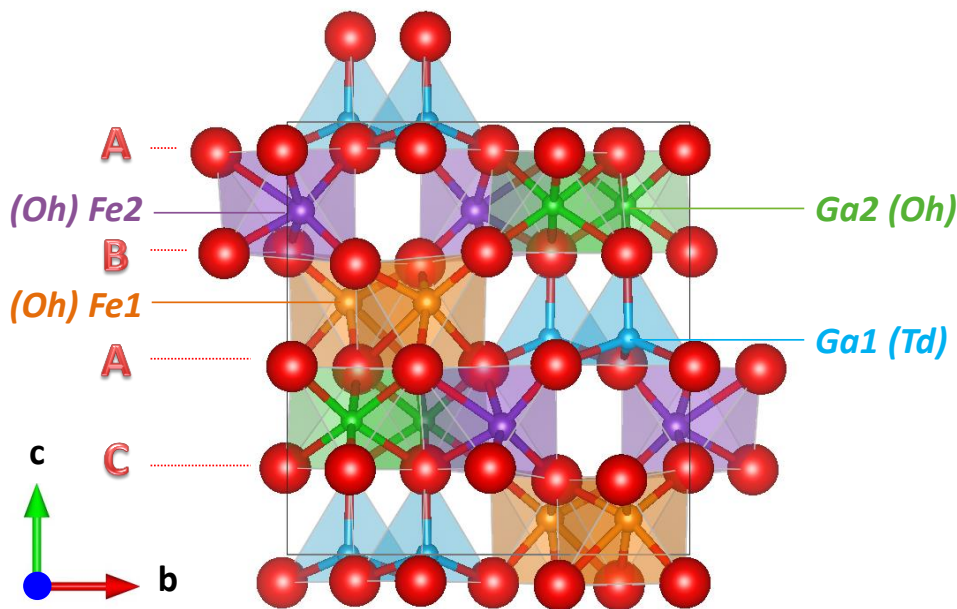
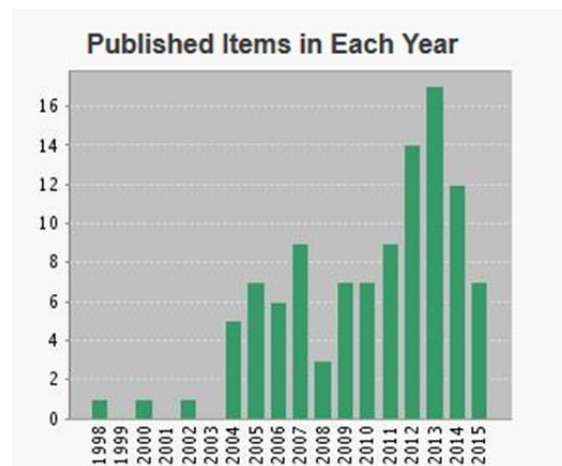
apport de la spectrométrie  
Mössbauer pour la caractérisation  
des couches minces

# une alternative à $\text{BiFeO}_3$ : $\text{GaFeO}_3$

$\text{BiFeO}_3$



$\text{GaFeO}_3$



**ferrimagnétique**  $T_C > RT$  for  $x \geq 1.3$

**magnétoélectrique**  $\alpha_{bc} \approx 1 \times 10^{-11} (\text{s/m})$

[Arima et al. PRB 70 064426 (2004)]

**polaire** polarisation **calculée**  
25  $\mu\text{C}/\text{cm}^2$  pour  $\text{GaFeO}_3$

[Stoeffler J. Phys.: Condens. Matter 24 (2012) 185502]

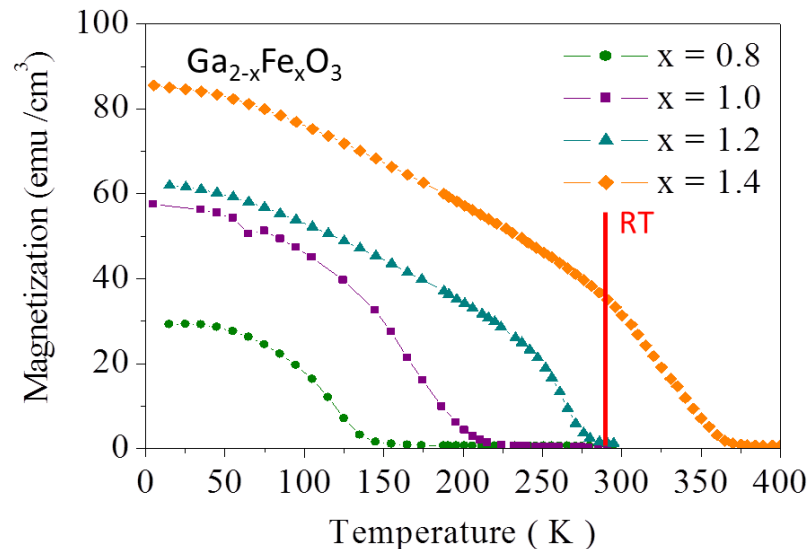
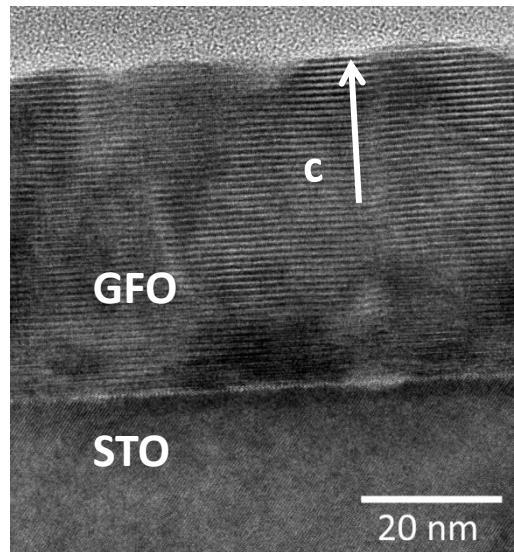
polarisation **mesurée**  
ca. 30  $\mu\text{C}/\text{cm}^2$  pour  $\text{Ga}_{0.9}\text{Fe}_{1.1}\text{O}_3$

[Kundys et al. J. Eur. Ceram. Soc. 35 (2015) 2277]

**non réversible en massif**

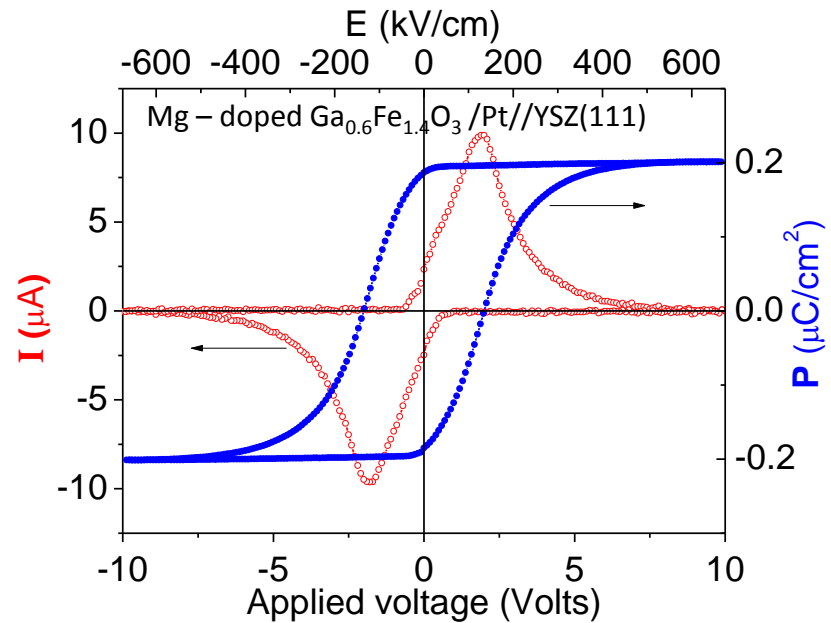
# GFO : un multiferroïque en couches minces ?

C. Ulhaq, IPCMS, Strasbourg

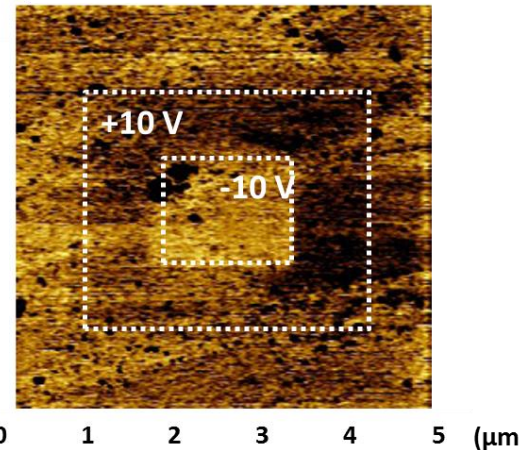


[Trassin et al., J. Mater. Chem. 19 (2009) 8876]

Coll S. Cherifi, IPCMS, Strasbourg



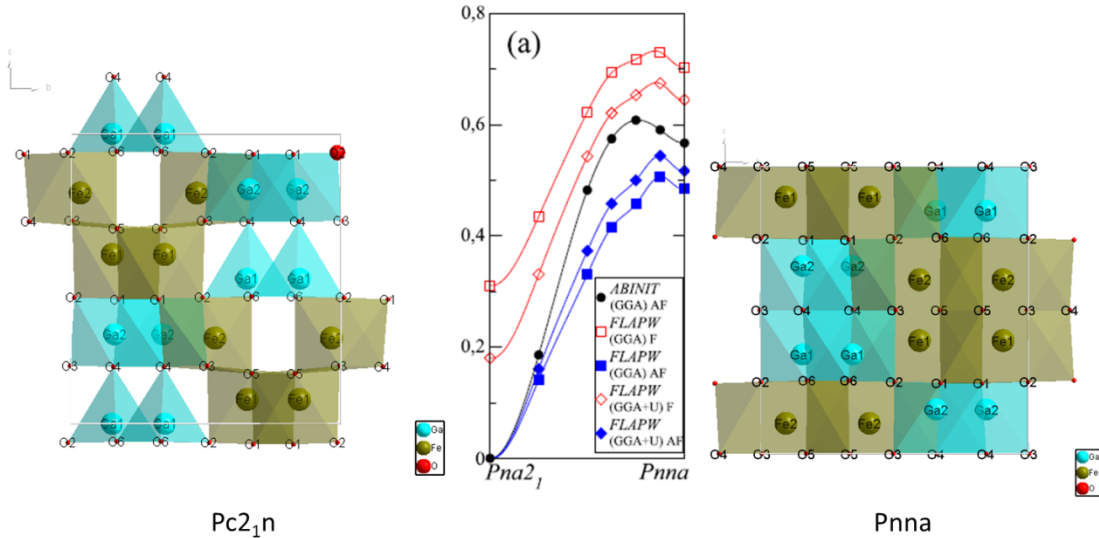
Coll. B. Gautier, INL, Lyon



[Thomasson et al.  
J. Appl. Phys. 113 (2013)  
214101]

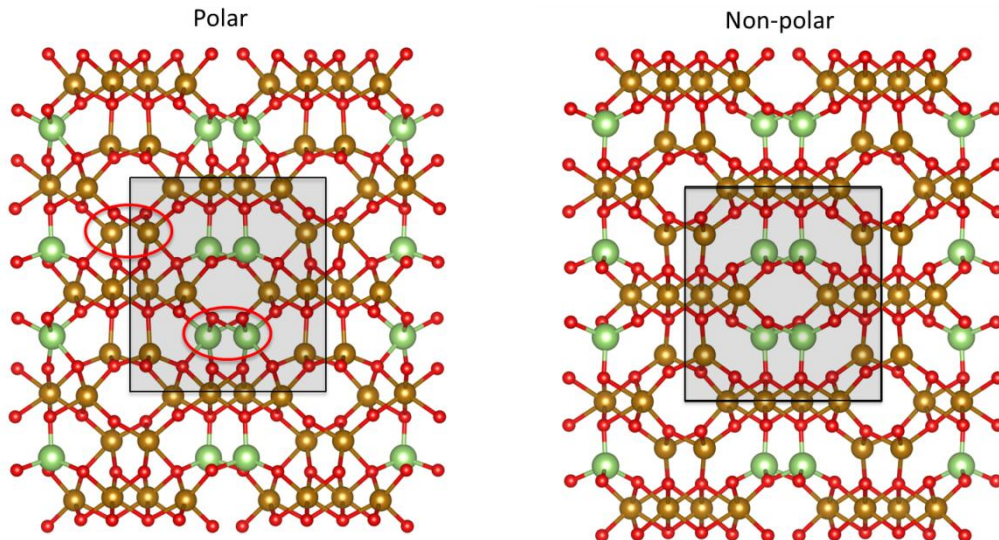
# GFO : un multiferroïque en couches minces ? Quel mécanisme ?

D. Stoeffler, IPCMS, Strasbourg



Coût énergétique trop élevé (0.5 eV)

Collaboration K.Z. Rushchanskii, S. Blügel and M. Ležaić, PGI, FZJ Jülich



Mécanisme proposé de coût énergétique plus faible reposant sur une distribution cationique particulière



# Importance de la distribution cationique

## Etude combinée spectroscopie ellipsométrique - DFT

Coll. M. Alouani, F. Ibrahim (IPCMS, Strasbourg)

S. Choi (Golden, Colorado, USA)

## Diffraction résonante des rayons X

[Thomasson et al. *RSC Adv.* 3 (2013) 3124-3130]

BM02 D2AM beamline  
(ESRF, Grenoble, France)



sensible à

- environnement atomique local de l'atome cible au travers des processus d'absorption
- l'ordre à longue portée au travers de la diffraction

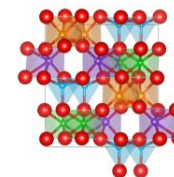
Coll. V. Favre-Nicolin  
(CEA Grenoble)

N. Boudet  
(Institut Néel, Grenoble)

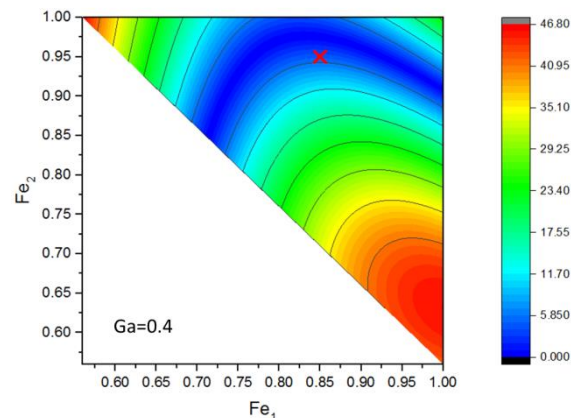
Y. Joly  
(Institut Néel, Grenoble)

Y. Wakabayashi  
(Osaka University, Japan)

Fe in	Ga1	Ga2	Fe1	Fe2
	0.40	0.75	0.85	0.95



distribution confirmée par  
**Mesures magnétiques / MFT**

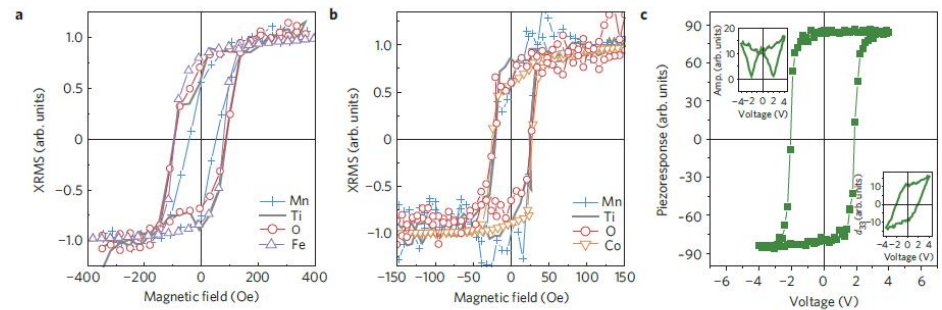


# Multiferroïques extrinsèques

## Interface-induced room-temperature multiferroicity in BaTiO<sub>3</sub>

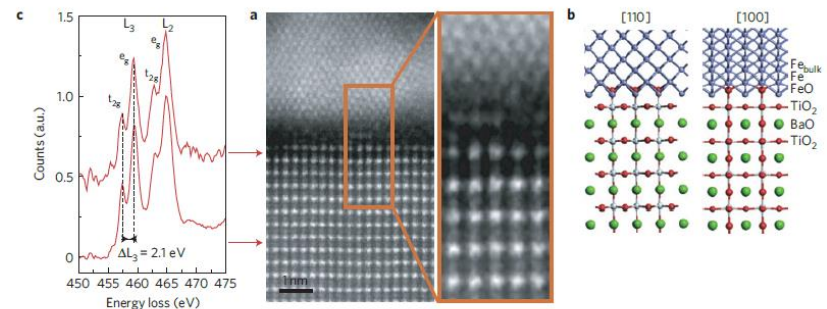
S. Valencia<sup>1</sup>, A. Crassous<sup>2</sup>, L. Bocher<sup>3</sup>, V. Garcia<sup>2</sup>, X. Moya<sup>4</sup>, R. O. Cherifi<sup>2</sup>, C. Deranlot<sup>2</sup>, K. Bouzehouane<sup>2</sup>, S. Fusil<sup>2,5</sup>, A. Zoubi<sup>3</sup>, A. Gloter<sup>3</sup>, N. D. Mathur<sup>4</sup>, A. Gaupp<sup>1</sup>, R. Abrudan<sup>6</sup>, F. Radu<sup>1</sup>, A. Barthélémy<sup>2</sup> and M. Bibes<sup>2</sup>★

Multiferroic materials possess two or more ferroic orders but have room-temperature examples. Those that are ferromagnetic and ferr storage if the ferroic orders switch independently, or in electric-field strong. Future applications could also exploit toroidal moments and of time-reversal and space-inversion symmetries. Here, we use soft X-ray microscopy to reveal that, at the interface with Fe or Co, ultrathin film possess a magnetization and a polarization that are both spontaneously calculated of realistic interface structures provide insight into the new approach for creating room-temperature multiferroics.



**Figure 3** | Evidence for room-temperature multiferroicity. **a**, XRMS versus H for Mn, Fe, Ti and O for the Fe/BTO sample. **b**, XRMS versus H for Mn, Co, Ti and O for the Co/BTO sample. **c**, Out-of-plane piezoelectric phase loop of a BTO(1.2 nm)/LSMO sample. The corresponding amplitude and extracted piezoelectric coefficient ( $d_{33}$ ) data are shown in the insets.

contrôle de la polarisation en spin  
des interfaces Fe/BTO et Co/BTO  
par direction de polarisation électrique de BTO  
moment magnétique et hystérèse dans BTO



**Figure 4** | Interface structure analysis. **a**, Atomically resolved HAADF image of the Fe/BTO interface of the Fe/BTO(50 nm)/LSMO(30 nm)//NGO(001) heterostructure. **b**, Structural model of the type II interface, that is,  $-\text{Fe}-\text{FeO}-\text{TiO}_2-\text{BaTiO}_3$ . **c**,  $\text{Ti L}_{2,3}$ -edge spectra acquired on  $\text{TiO}_2$  columns located in the BTO layer (blue line) and next to the Fe layer (red line).

# Multiferroïques extrinsèques

PHYSICAL REVIEW B **88**, 121409(R) (2013)

## Strong magnetoelectric coupling in multiferroic Co/BaTiO<sub>3</sub> thin films

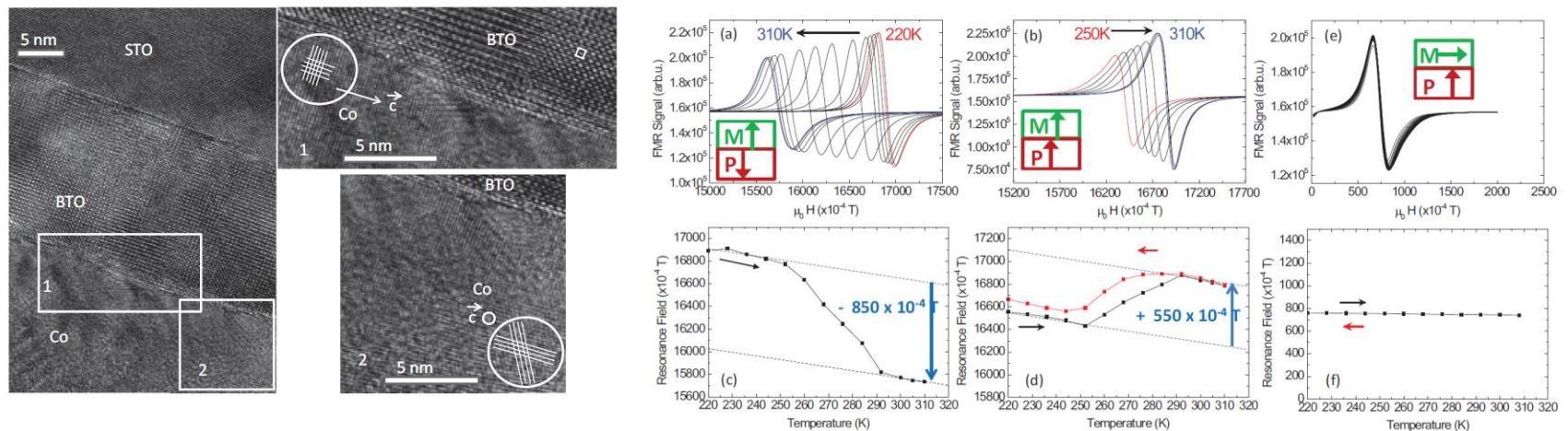
N. Jedrecy,<sup>1,\*</sup> H. J. von Bardeleben,<sup>1</sup> V. Badjeck,<sup>1</sup> D. Demaille,<sup>1</sup> D. Stanesco,<sup>2</sup> H. Magnan,<sup>2</sup> and A. Barbier<sup>2</sup>

<sup>1</sup>Institut des Nano Sciences de Paris, UPMC-Sorbonne Universités, CNRS-UMR7588, 4 Place Jussieu, 75252 Paris Cedex 05, France

<sup>2</sup>CEA, IRAMIS, SPCSI, F-91191 Gif-sur-Yvette Cedex, France

(Received 24 July 2013; published 23 September 2013)

We have found evidence for a strong magnetoelectric (ME) coupling at room temperature between polycrystalline Co layers (5–40 nm) and single-crystalline (001)-oriented BaTiO<sub>3</sub> layers (15–17 nm). We took advantage of the quasi-single polarization orientation, perpendicular to the film plane, of the ferroelectric BaTiO<sub>3</sub> domains in the tetragonal phase. Using ferromagnetic resonance spectroscopy with the Co magnetization aligned either parallel or antiparallel to the BaTiO<sub>3</sub> polarization, we assessed a strong anisotropy of about 0.14 T in the Co resonance field positions, indicating a coupling constant of 0.27 s/F. When sweeping the temperature through the phase transitions of BaTiO<sub>3</sub>, the two resonance positions are shifted in opposite directions. The ME coupling induces a notable magnetic anisotropy resulting in high values of the out-of-plane remanent magnetization. Our results are promising for future multiferroic devices.



le comportement de Co suit les changements de structure de BTO (FMR)

# Multiferroïques extrinsèques



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Multiferroic materials and heterostructures / Matériaux et hétérostructures multiferroïques

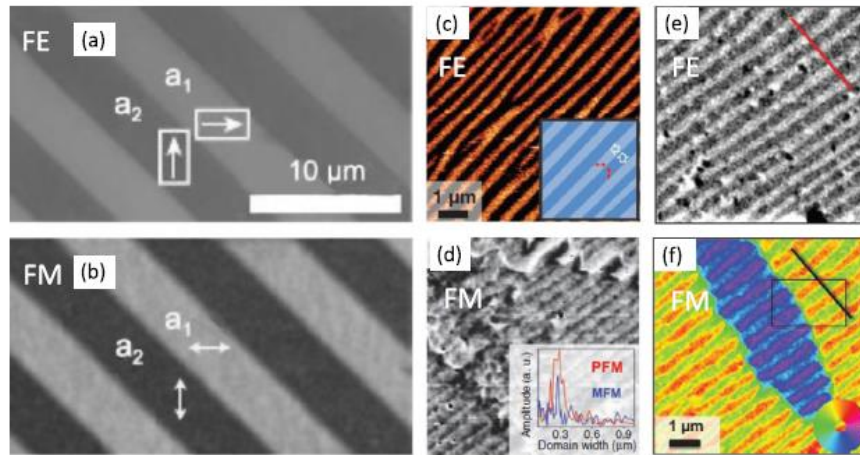
## Domains and domain walls in multiferroics

### *Domaines et parois de domaines dans les multiferroïques*

Sylvia Matzen<sup>a</sup>, Stéphane Fusil<sup>b,\*</sup>

<sup>a</sup> Institut d'électronique fondamentale, Bat. 220, Université Paris-Sud, UMR 8622, CNRS, 91405 Orsay, France

<sup>b</sup> Unité mixte de physique CNRS/Thales, campus de l'École polytechnique, 1, avenue Augustin-Fresnel, 91767 Palaiseau, France



**Fig. 2.** (Color online.) Ferroelectric/magnetic bilayers ( $\text{CoFe}/\text{BaTiO}_3$  and  $\text{CoFe}/\text{BiFeO}_3$ ).  $\text{Co}_{0.6}\text{Fe}_{0.4}/\text{BaTiO}_3$  with ferroelastic coupling: Polarization microscopy images of the ferroelectric (a) and ferromagnetic (b) domain structures. The arrows indicate the polarization direction in the BTO substrate and the orientation of the uniaxial magnetic easy axes in the CoFe film deposited on top; after Lahtinen et al. [28].  $\text{Co}_{0.9}\text{Fe}_{0.1}/\text{BiFeO}_3$  with interfacial exchange coupling: PFM image showing the FE stripes like domains in  $\text{BiFeO}_3$  (c). MFM image of the  $\text{Co}_{0.9}\text{Fe}_{0.1}$  on top with stripe like magnetic contrast of the same periodicity (d). Backscattered electron contrast imaging of the FE domains in  $\text{BiFeO}_3$  (e) and scanning electron microscopy with polarization analysis (SEMPA) showing the imprinted FM domains in  $\text{Co}_{0.9}\text{Fe}_{0.1}$  (f); after Trassin et al. [30].



Etude des couplages interfaciaux

Recherche de la compréhension des propriétés dynamiques des parois de domaines

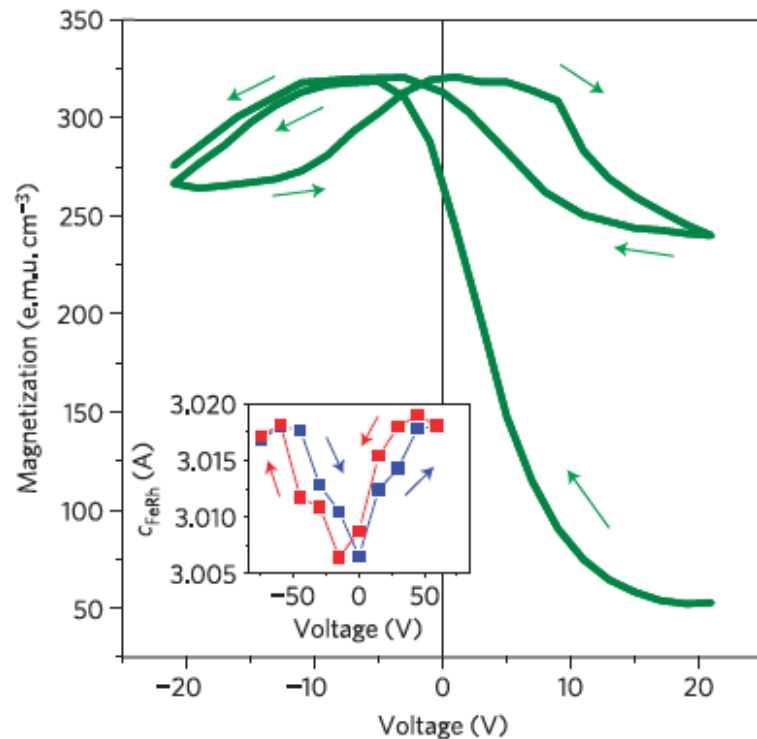
Techniques de microscopie permettant la visualisation directe des domaines ferroélectriques et ferromagnétiques à l'échelle nanométrique (PEEEM, PFM, MFM...)

# Effets de contrainte et de champ

contrôle de l'ordre magnétique par un champ électrique : le cas de FeRh/BaTiO<sub>3</sub>

## Electric-field control of magnetic order above room temperature

R. O. Cherifi<sup>1†</sup>, V. Ivanovskaya<sup>1†</sup>, L. C. Phillips<sup>1</sup>, A. Zobelli<sup>2</sup>, I. C. Infante<sup>3</sup>, E. Jacquet<sup>1</sup>, V. Garcia<sup>1</sup>, S. Fusil<sup>1,4</sup>, P. R. Briddon<sup>5</sup>, N. Guiblin<sup>3</sup>, A. Mougin<sup>2</sup>, A. A. Ünal<sup>6</sup>, F. Kronast<sup>6</sup>, S. Valencia<sup>6</sup>, B. Dkhil<sup>3</sup>, A. Barthélémy<sup>1</sup> and M. Bibes<sup>1\*</sup>



Controlling magnetism by means of electric fields is a key issue for the future development of low-power spintronics<sup>1</sup>. Progress has been made in the electrical control of magnetic anisotropy<sup>2</sup>, domain structure<sup>3,4</sup>, spin polarization<sup>5,6</sup> or critical temperatures<sup>7,8</sup>. However, the ability to turn on and off robust ferromagnetism at room temperature and above has remained elusive. Here we use ferroelectricity in BaTiO<sub>3</sub> crystals to tune the sharp metamagnetic transition temperature of epitaxially grown FeRh films and electrically drive a transition between antiferromagnetic and ferromagnetic order with only a few volts, just above room temperature. The detailed analysis of the data in the light of first-principles calculations indicate that the phenomenon is mediated by both strain and field effects from the BaTiO<sub>3</sub>. Our results correspond to a magnetoelectric coupling larger than previous reports by at least one order of magnitude and open new perspectives for the use of ferroelectrics in magnetic storage and spintronics.

nature  
materials

LETTERS

PUBLISHED ONLINE: 26 JANUARY 2014 | DOI: 10.1038/NMAT3870

# Couplage ferroélectrique - supraconducteur

JOURNAL OF APPLIED PHYSICS **113**, 024910 (2013)



## BiFeO<sub>3</sub>/YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> heterostructures for strong ferroelectric modulation of superconductivity

A. Crassous,<sup>1</sup> R. Bernard,<sup>1</sup> S. Fusil,<sup>1,2</sup> K. Bouzehouane,<sup>1</sup> J. Briatico,<sup>1</sup> M. Bibes,<sup>1</sup>  
A. Barthélémy,<sup>1</sup> and Javier E. Villegas<sup>1,a)</sup>

<sup>1</sup>Unité Mixte de Physique CNRS/Thales, 1 Ave. A. Fresnel, 91767 Palaiseau, and Université Paris Sud 11, 91405 Orsay, France

<sup>2</sup>Université d'Evry-Val d'Essonne, Boulevard François Mitterrand, 91025 Evry, France

(Received 27 July 2012; accepted 17 December 2012; published online 11 January 2013)

We describe the growth, structural, and functional characterization of BiFeO<sub>3</sub>/YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> ferroelectric/superconductor heterostructures. High-structural display good ferroelectric and superconducting properties. We field-effect modulation of the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> superconducting upon ferroelectric switching of the BiFeO<sub>3</sub> overlayer, and we reversible. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3644441>]

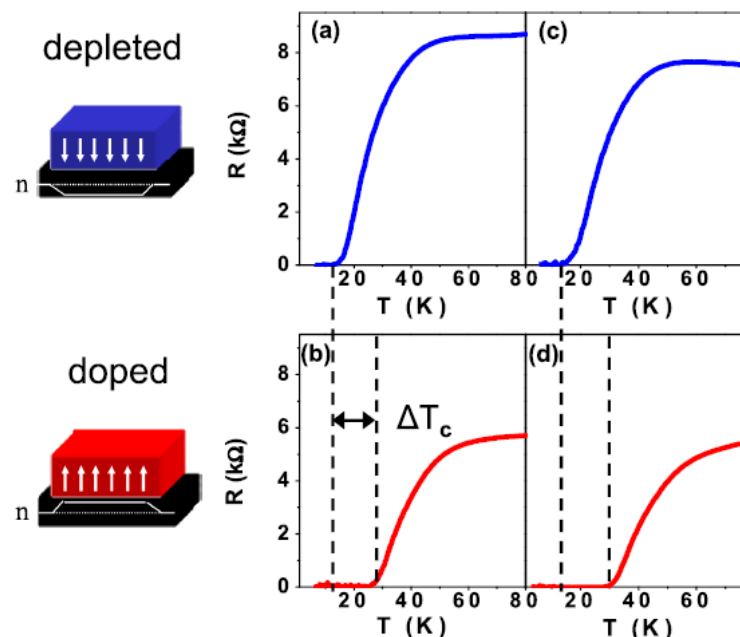


FIG. 4. Resistance versus temperature for a BFO(30nm)/YBCO (4 u.c.)/PBCO(2.4nm)//STO heterostructure in the “as-grown” state (a), and after subsequently reversing the ferroelectric polarization outwards (b), towards (c), and outwards (d) the YBCO layer. The sketch indicates the direction of the ferroelectric polarization and the expected variation in the carrier density within the YBCO layer.

Contrôle de la supraconductivité par un champ électrique

# Field-effect control of superconductivity and Rashba spin-orbit coupling in top-gated $\text{LaAlO}_3/\text{SrTiO}_3$ devices

S. Hurand<sup>1</sup>, A. Jouan<sup>1</sup>, C. Feuillet-Palma<sup>1</sup>, G. Singh<sup>1</sup>, J. Biscaras<sup>1</sup>, E. Lesne<sup>2</sup>, N. Reyren<sup>2</sup>, A. Barthélémy<sup>2</sup>, M. Bibes<sup>2</sup>, J. E. Villegas<sup>2</sup>, C. Ulysse<sup>3</sup>, X. Lafosse<sup>3</sup>, M. Pannetier-Lecoeur<sup>4</sup>, S. Caprara<sup>5</sup>, M. Grilli<sup>5</sup>, J. Lesueur<sup>1</sup> & N. Bergeal<sup>1</sup>

The recent development in the fabrication of artificial oxide heterostructures opens new avenues in the field of quantum materials by enabling the manipulation of the charge, spin and orbital degrees of freedom. In this context, the discovery of two-dimensional electron gases (2-DEGs) at  $\text{LaAlO}_3/\text{SrTiO}_3$  interfaces, which exhibit both superconductivity and strong Rashba spin-orbit coupling (SOC), represents a major breakthrough. Here, we report on the realisation of a field-effect  $\text{LaAlO}_3/\text{SrTiO}_3$  device, whose physical properties, including superconductivity and SOC, can be tuned over a wide range by a top-gate voltage. We derive a phase diagram, which emphasises a field-effect-induced superconductor-to-insulator quantum phase transition. Magneto-transport measurements show that the Rashba coupling constant increases linearly with the interfacial electric field. Our results pave the way for the realisation of mesoscopic devices, where these two properties can be manipulated on a local scale by means of top-gates.

SCIENTIFIC REPORTS 

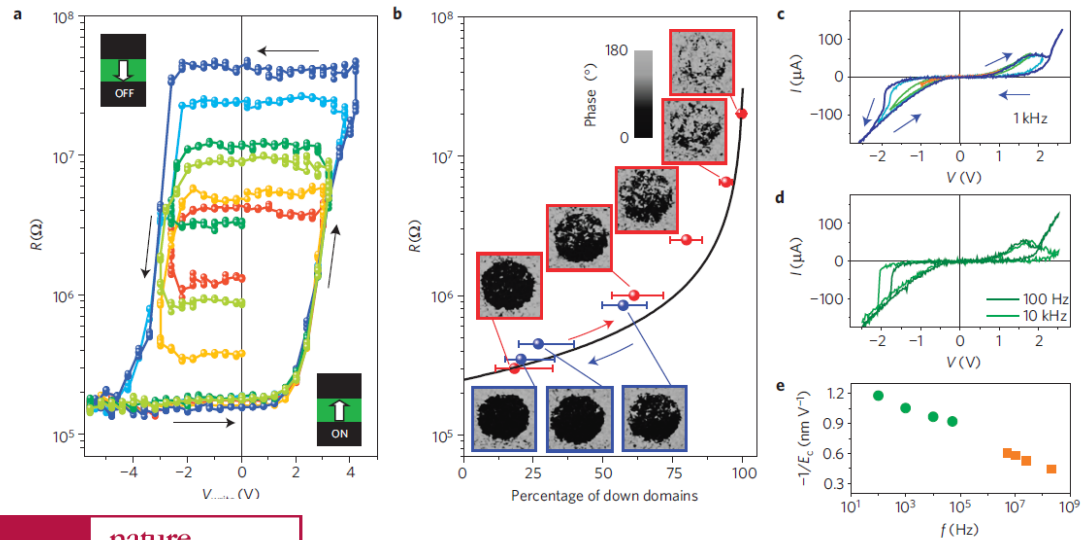
# Memristors – des synapses électroniques

## A ferroelectric memristor

André Chanthbouala<sup>1</sup>, Vincent Garcia<sup>1</sup>, Ryan O. Cherifi<sup>1</sup>, Karim Bouzehouane<sup>1</sup>, Stéphane Fusil<sup>1,2</sup>, Xavier Moya<sup>3</sup>, Stéphane Xavier<sup>4</sup>, Hiroyuki Yamada<sup>1,5</sup>, Cyrille Deranlot<sup>1</sup>, Neil D. Mathur<sup>3</sup>, Manuel Bibes<sup>1</sup>, Agnès Barthélémy<sup>1\*</sup> and Julie Grollier<sup>1</sup>

Memristors are continuously tunable resistors that emulate biological synapses<sup>1,2</sup>. Conceptualized in the 1970s, they traditionally operate by voltage-induced displacements of matter, although the details of the mechanism remain under debate<sup>3-5</sup>. Purely electronic memristors based on well-established physical phenomena with albeit modest resistance changes have also emerged<sup>6,7</sup>. Here we demonstrate the domain configurations in ferroelectric tunnel junction memristive behaviour with resistance variations of several orders of magnitude and a 10 ns operation time. The quasi-continuous resistance variation and the analytical expression for the memristive behaviour suggest new opportunities for ferroelectric memristors as the basis of future neuromorphic computing.

BaTiO<sub>3</sub>(2 nm) /  
La<sub>0.67</sub>Sr<sub>0.33</sub>MnO<sub>3</sub>  
(30 nm) (BTO/LSMO)



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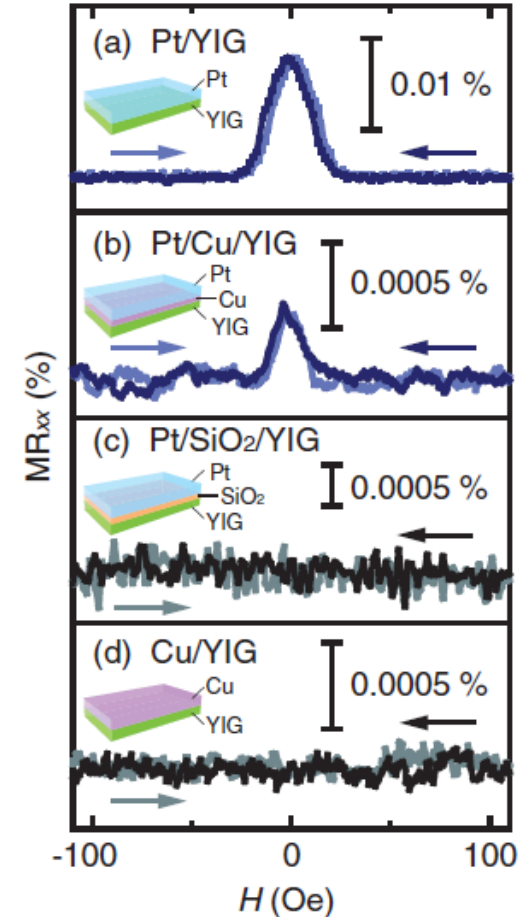
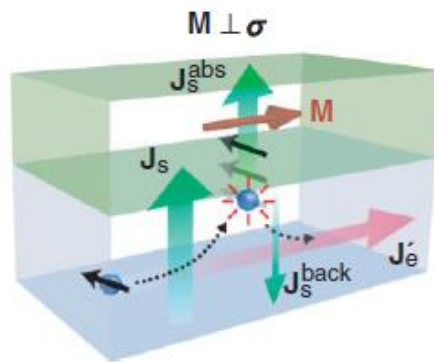
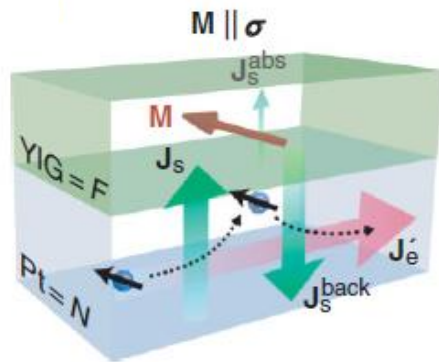
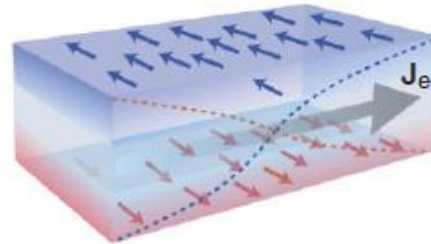
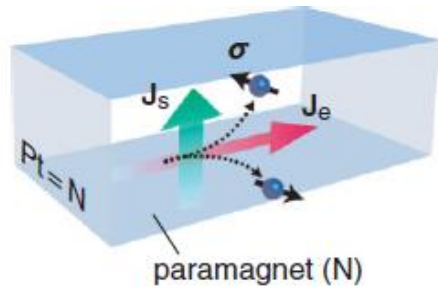
PUBLISHED ONLINE: 16 SEPTEMBER 2012 | DOI:10.1038/NMAT3415

nature  
materials



# Perspectives : le couplage spin-orbite

Effet Hall de spin : des systèmes (Pt/YIG, ...)



[Nakayama et al. PRL 110 (2013) 206601]

Des matériaux :  $\text{Sr}_2\text{IrO}_4$

# Une communauté soutenue par des GDR

## **OXYFUN : Oxydes fonctionnels : du matériau au dispositif**

**les oxydes fonctionnels, depuis le matériau jusqu'au dispositif**

Catherine DUBOURDIEU (INL, Lyon) , Wilfrid PRELLIER (CRISMAT, Caen)

## **MICO : Matériaux et interactions en compétition**

**matériaux à fortes corrélations électroniques**

Marie-Bernadette LEPETIT (Institut Néel, Grenoble), Pascale FOURY (LPS, Orsay)

## **MEETICC : Matériaux, Etats Electroniques et Couplages**

**non-Conventionnels**

**favoriser les rencontres entre physiciens et chimistes sur les systèmes corrélés, phases topologiques et systèmes confinés**

Pascale FOURY (LPS, Orsay), Etienne JANOD (IMN, Nantes)