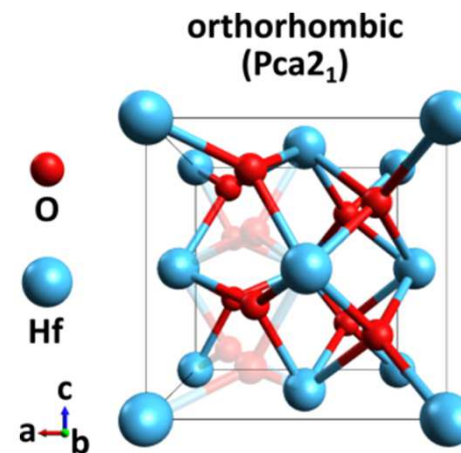


# Intrinsic and Extrinsic Factors Behind the Large Remanent Polarization of La:HfO<sub>2</sub>

T. Schenk<sup>1,2</sup>, C. M. Fancher<sup>3</sup>, M. H. Park<sup>1,4</sup>, C. Richter<sup>1</sup>,  
C. Künneth<sup>5</sup>, A. Kersch<sup>5</sup>, J. L. Jones<sup>6</sup>, T. Mikolajick<sup>1</sup>,  
U. Schroeder<sup>1</sup>



<sup>1</sup> NaMLab gGmbH/TU Dresden, Noethnitzer Str. 64, D-01187 Dresden, Germany

<sup>2</sup> Luxembourg Institute of Science and Technology (LIST), 41 Rue du Brill, L-4422 Belvaux, Luxembourg

<sup>3</sup> Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA

<sup>4</sup> Pusan National University, 2, Busandaehak-ro 63beon-gil, Geumjeong-gu, Busan, 46241, Republic of Korea

<sup>5</sup> Munich University of Applied Sciences, Lothstr. 34, D-80335 Munich, Germany

<sup>6</sup> North Carolina State University, Raleigh, North Carolina 27695-7907, USA

# Outline

Introduction

Basic Experimental Data & Theory

Stress/Texture from XRD

Summary and Outlook

# Outline

Introduction

Basic Experimental Data & Theory

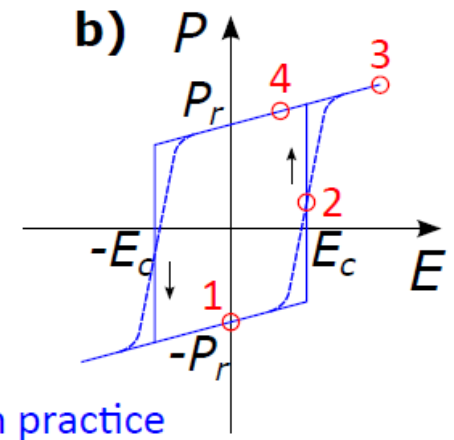
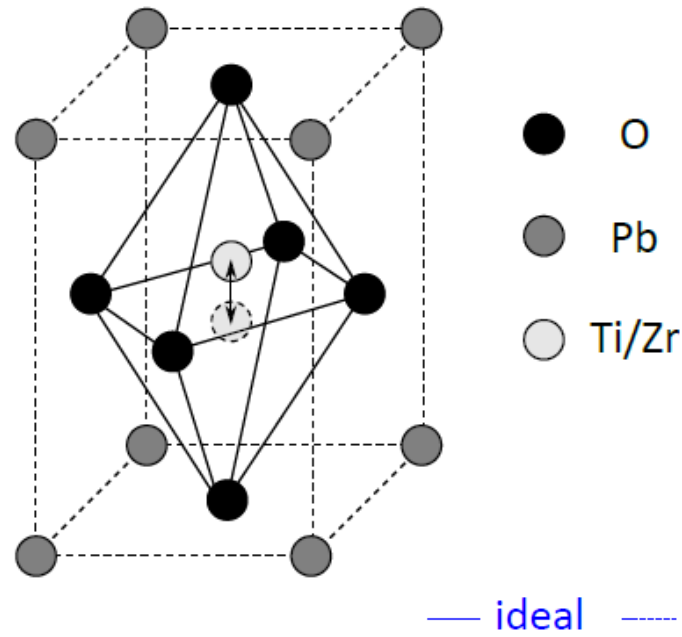
Stress/Texture from XRD

Summary and Outlook

# Introduction

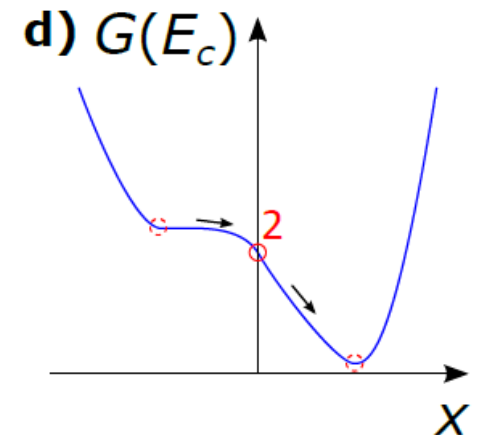
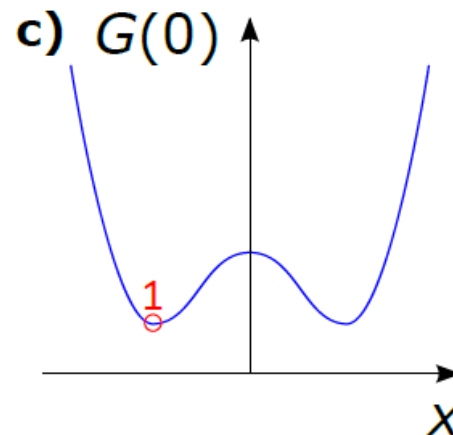
## Ferroelectricity

- permanent dipole  
→ polar phase
- double-well potential
- can be switched by electric field



## Classic Ferroelectrics

- PZT:  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$
- BTO:  $\text{BaTiO}_3$
- BFO:  $\text{BiFeO}_3$

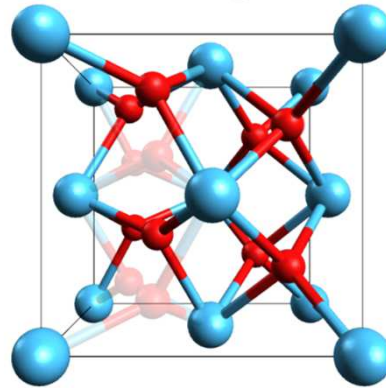


# Introduction

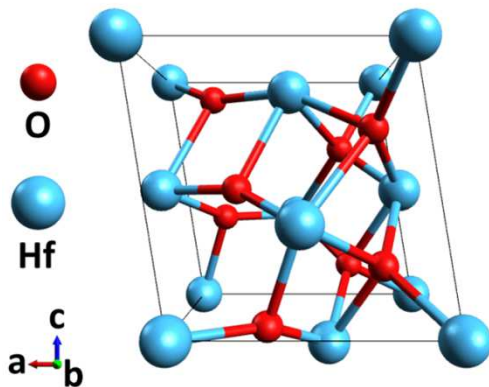
## Relevant Phases in $\text{HfO}_2$

FE orth. phase

orthorhombic  
( $\text{Pca2}_1$ )



monoclinic  
( $\text{P2}_1/\text{c}$ )

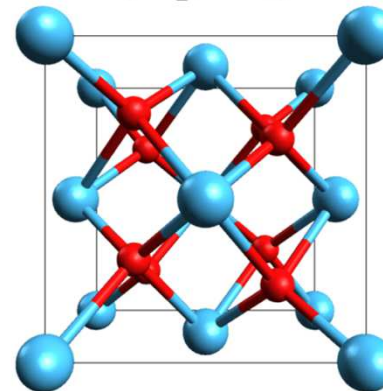


bulk phase, lower  $k$  ( $\approx 20$ )

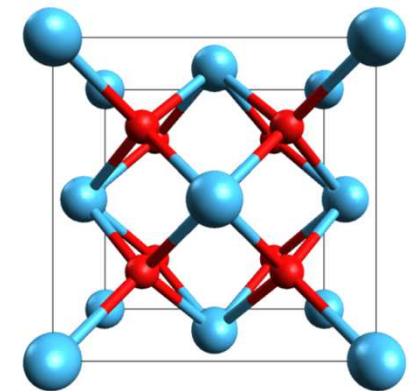
“doping” with  
e.g. Si



tetragonal  
( $\text{P4}_2/\text{nmc}$ )

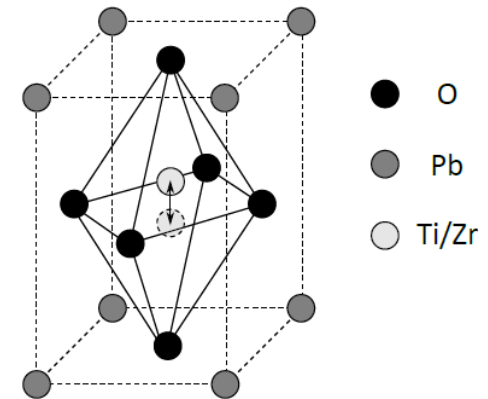


cubic  
( $\text{Fm3m}$ )



high  $T$  phases, higher  $k$  ( $> 30$ )

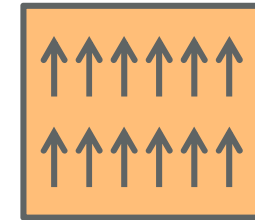
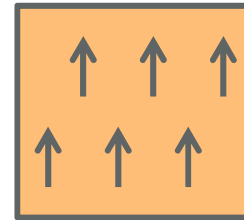
perovskite phase (tetra.)



# Introduction

**What determines the macroscopically effective Polarization?**

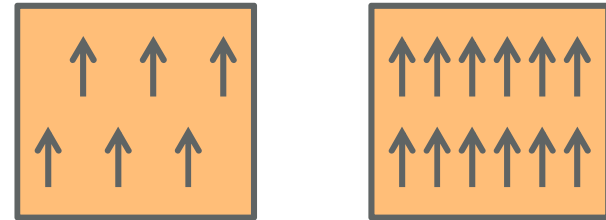
- volume density of dipoles:  
→ **phase composition**



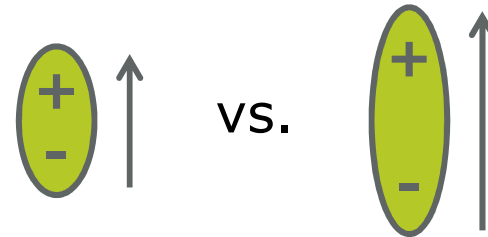
# Introduction

**What determines the macroscopically effective Polarization?**

- volume density of dipoles:  
→ **phase composition**



- length of the dipoles:  
→ **doping/stress**



# Introduction

**What determines the macroscopically effective Polarization?**

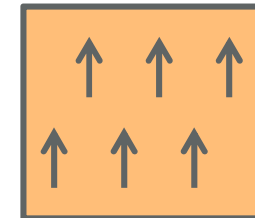
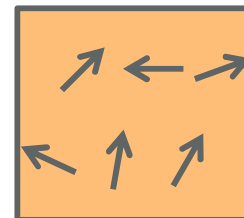
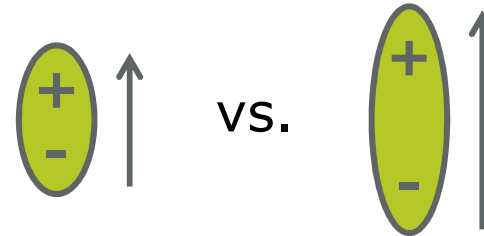
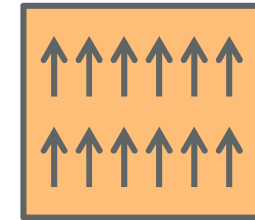
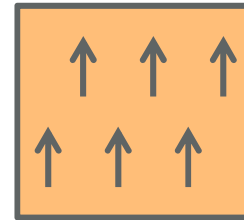
- volume density of dipoles:  
→ **phase composition**

**intrinsic**

- length of the dipoles:  
→ **doping/stress**

**extrinsic**

- orientation of the dipoles:  
→ **texture**



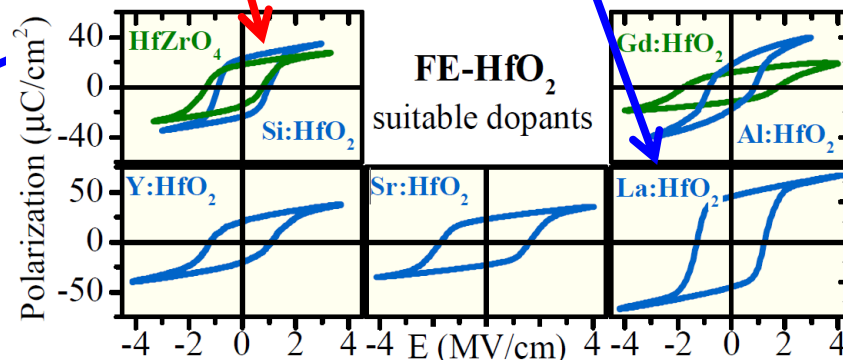
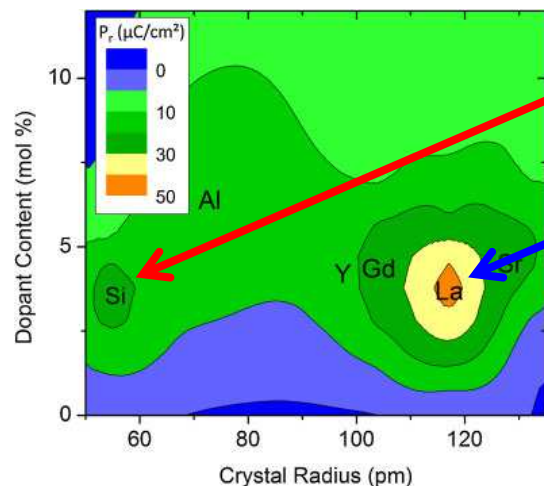


# Introduction

**Si:HfO<sub>2</sub> vs. La:HfO<sub>2</sub>**



**“Original vs. Rockstar”**



## FULL PAPER

Ferroelectrics

ADVANCED  
ELECTRONIC  
MATERIALS  
www.advelectronicmat.de

Inorganic Chemistry

Cite This: *Inorg. Chem.* 2018, 57, 2752–2765

Article  
pubs.acs.org/IC

## Si Doped Hafnium Oxide—A “Fragile” Ferroelectric System

Claudia Richter, Tony Schenk, Min Hyuk Park, Franziska A. Tschardtke, Everett D. Grimley, James M. LeBeau, Chuanchen Zhou, Chris M. Fancher, Jacob L. Jones, Thomas Mikolajick, and Uwe Schroeder\*

## Lanthanum-Doped Hafnium Oxide: A Robust Ferroelectric Material

Uwe Schroeder,<sup>\*,†</sup> Claudia Richter,<sup>†</sup> Min Hyuk Park,<sup>†</sup> Tony Schenk,<sup>†</sup> Milan Pešić,<sup>†</sup> Michael Hoffmann,<sup>†</sup> Franz P. G. Fengler,<sup>†</sup> Darius Pohl,<sup>‡</sup> Bernd Rellinghaus,<sup>‡</sup> Chuanchen Zhou,<sup>§</sup> Ching-Chang Chung,<sup>§</sup> Jacob L. Jones,<sup>§</sup> and Thomas Mikolajick<sup>†,||</sup>

U. Schroeder et al., *Jpn. J. Appl. Phys.* 2014, DOI: 10.7567/JJAP.53.08LE02  
J. Müller et al., *IEDM 2013*, DOI: 10.1109/IEDM.2013.6724605

# Outline

Introduction

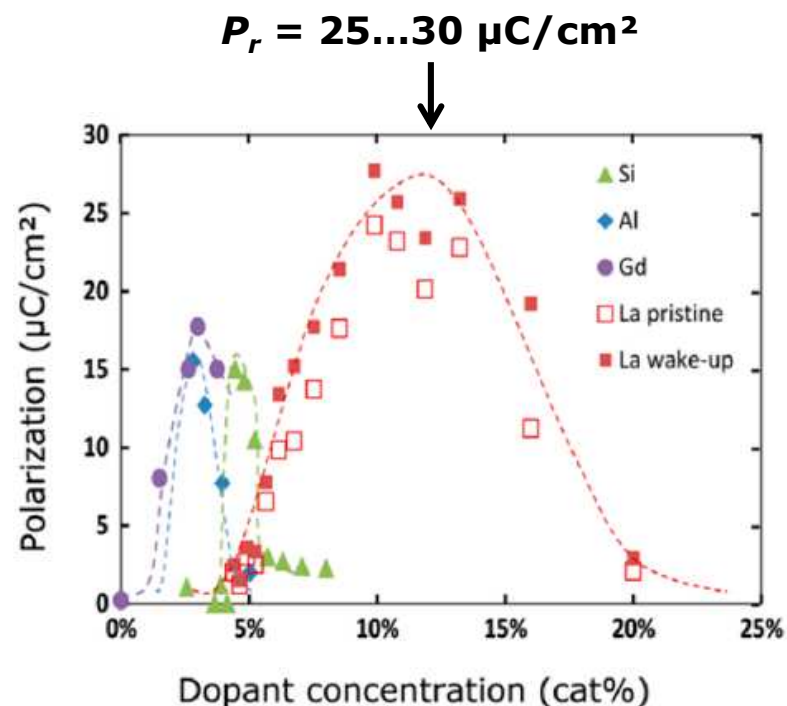
Basic Experimental Data & Theory

Stress/Texture from XRD

Summary and Outlook

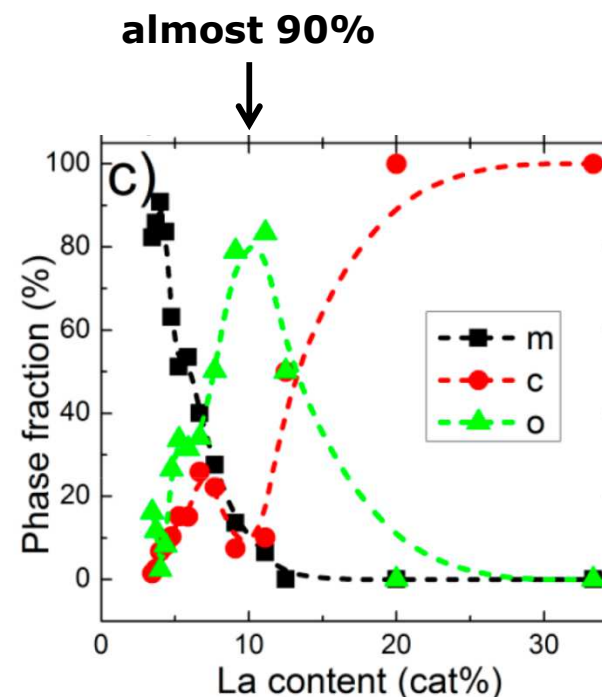
# Basic Experimental Data & Theory

## Electrical Measurements



- wide range of ferroelectricity
- high remanent polarization  $P_r$

## GIXRD: Rietveld Refinement



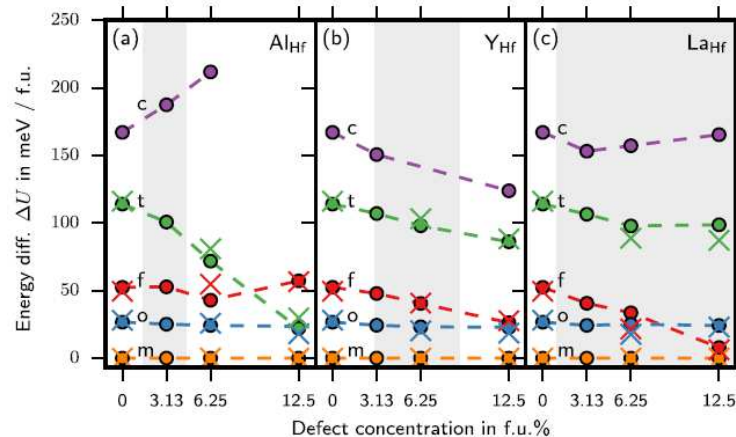
- high fraction of FE phase
- but similar values have been shown for other dopants

U. Schroeder et al. Inorg. Chem. 2018, DOI: 10.1021/acs.inorgchem.7b03149

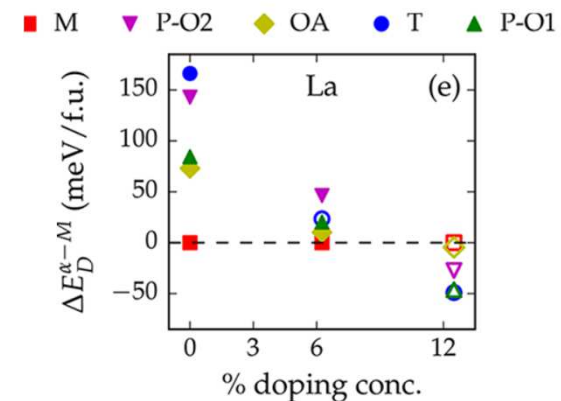
# Basic Experimental Data & Theory

## Density Functional Theory

- La is a very suitable stabilizer of the FE phase (bulk stability possible?)



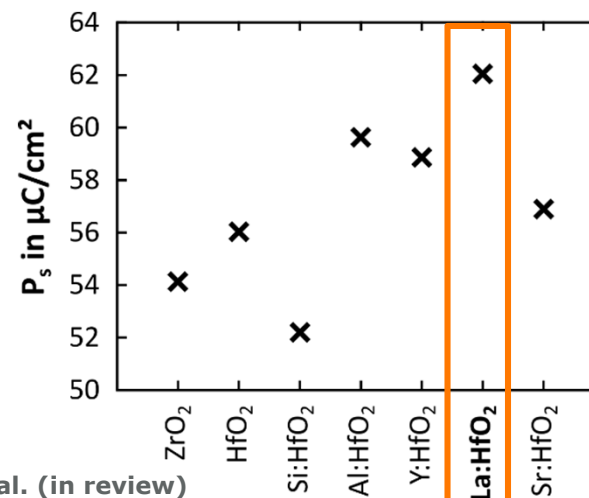
R. Materlik et al. J. Appl. Phys., DOI: 10.1063/1.5021746



R. Batra et al. Chem. Mater. 2017, DOI: 10.1021/acs.chemmater.7b02835

- So, what about the induced spontaneous polarization?

→ 62 vs. 52 – 60  $\mu\text{C}/\text{cm}^2$



T. Schenk et al. (in review)

# Outline

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Stress/Texture from XRD

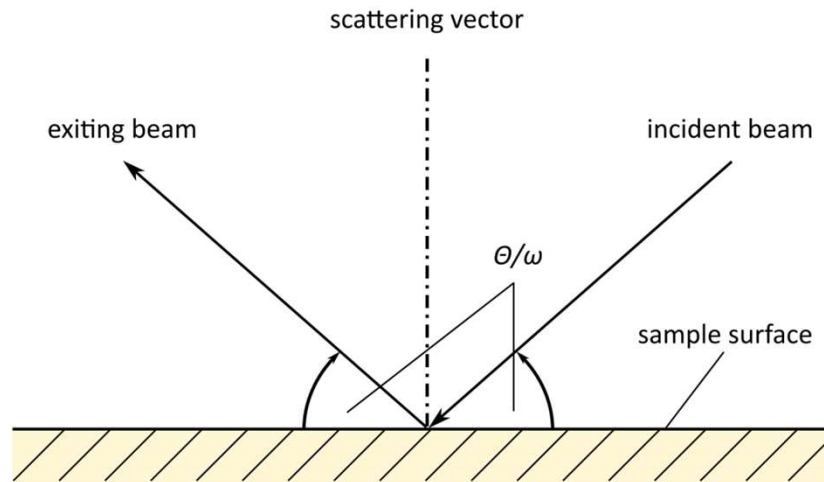
Summary and Outlook

# Stress/Texture from XRD

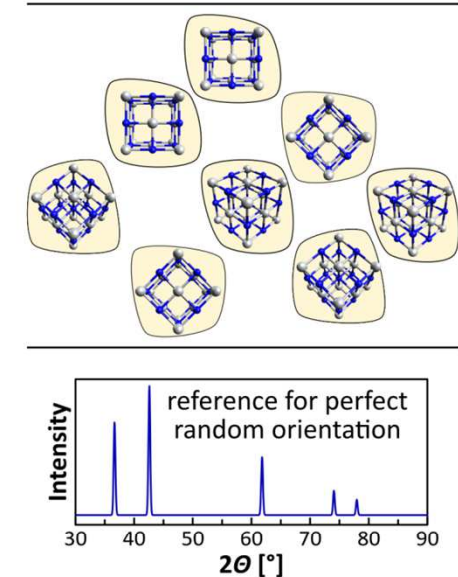
## Texture

- preferential orientation

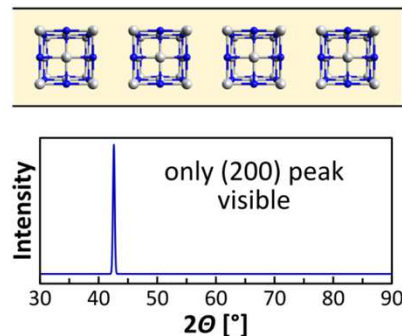
a) XRD in Bragg-Brentano geometry



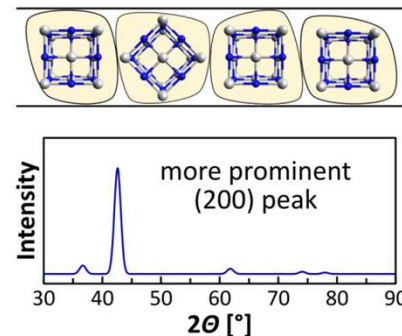
b) powder



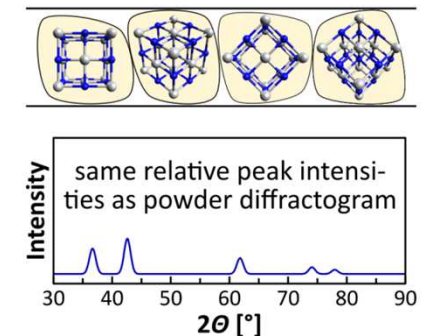
e) single crystal



d) (100)-textured film



c) non-textured film

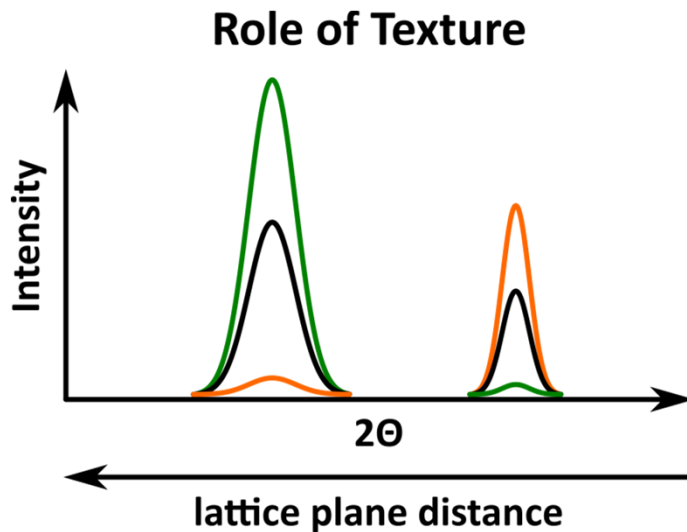


← increasing degree of texture

# Stress/Texture from XRD

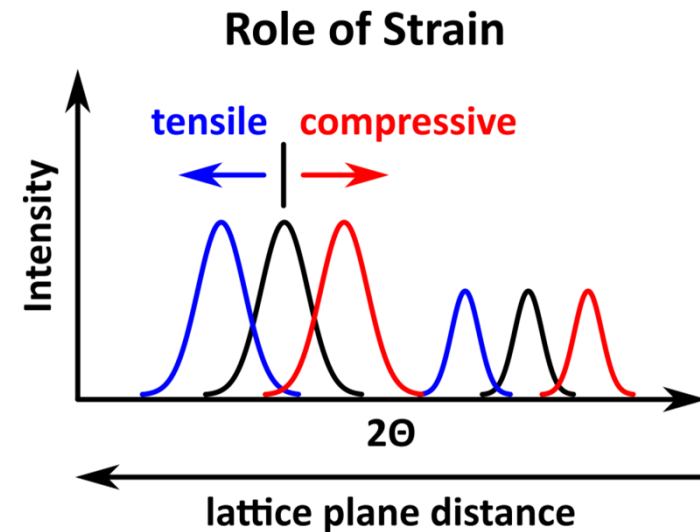
## Texture → Peak Intensity

- number of correctly oriented grains toward scattering vector



## Strain → Peak Position

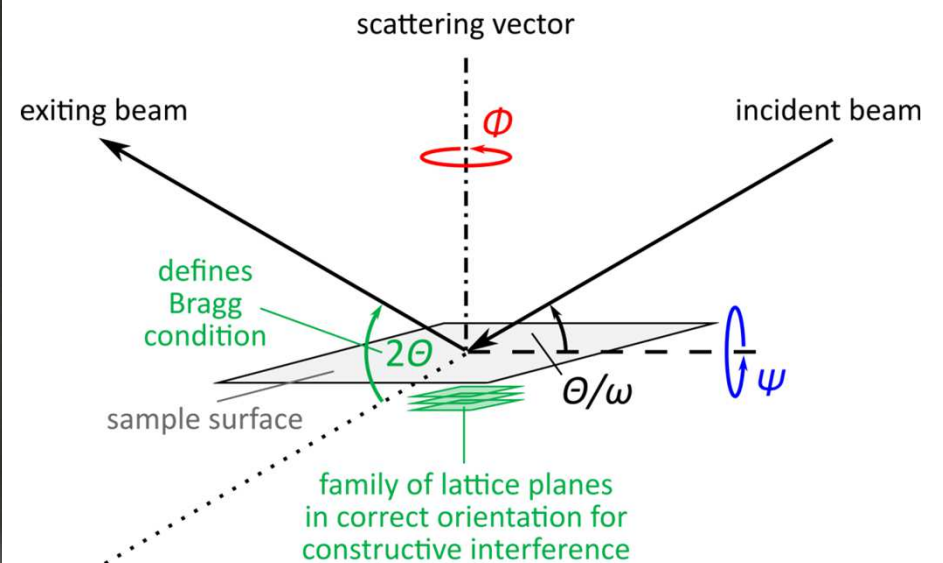
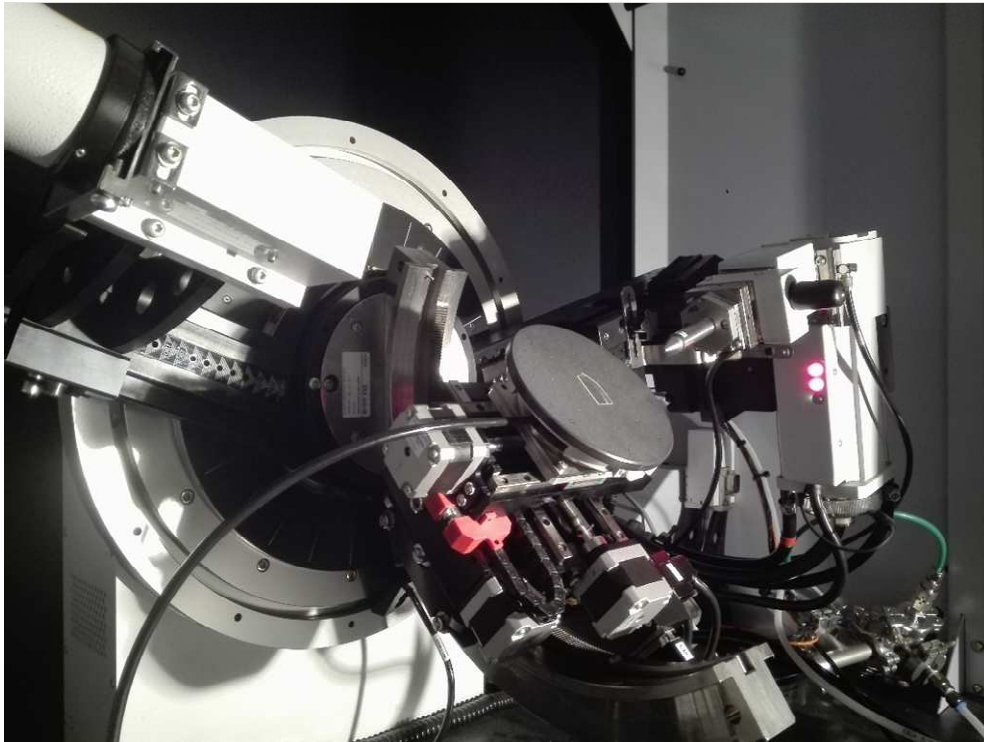
- Bragg equation:  $n \cdot \lambda = 2d \cdot \sin(\theta)$





# Stress/Texture from XRD

## Standard Lab XRD with Eulerian Cradle



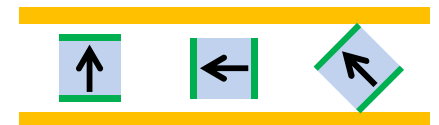
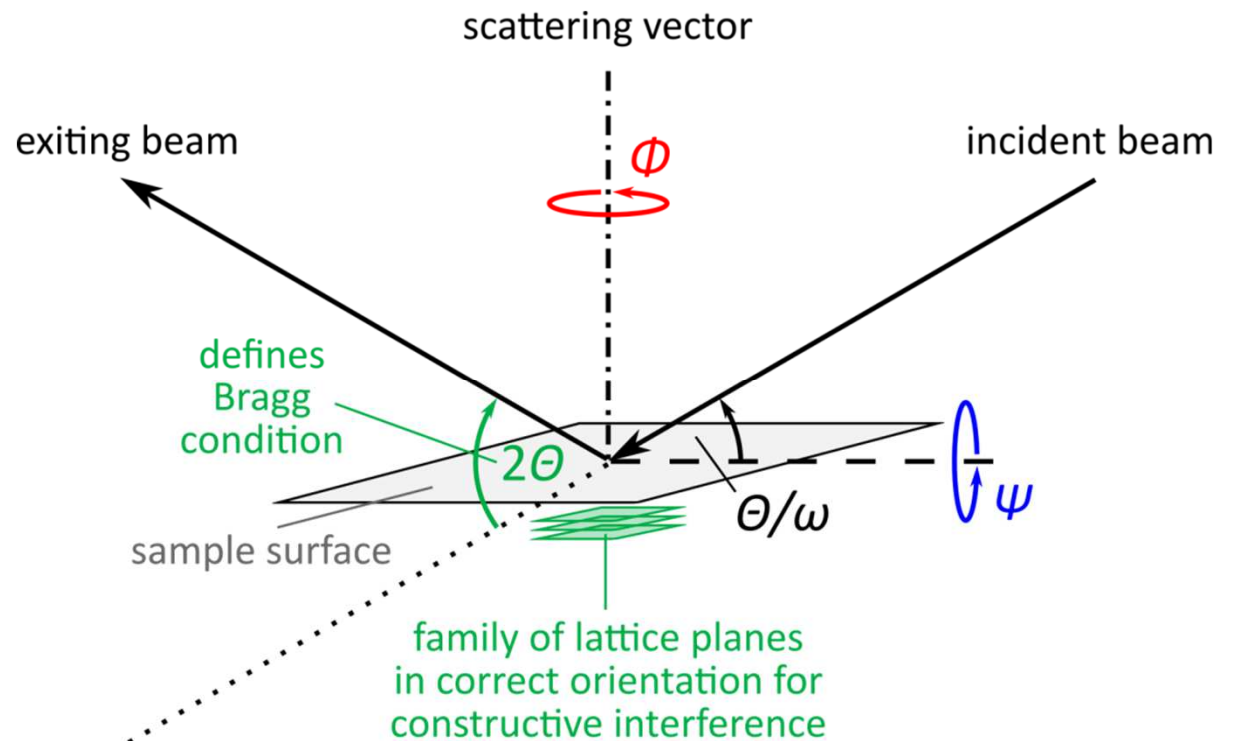
T. Schenk, PhD thesis, TU Dresden



# Stress/Texture from XRD

**2Theta  $2\theta$  / theta  $\theta$  / omega  $\omega$**

- define conditions for constructive interference in Bragg equation
- occurrence of peaks



T. Schenk, PhD thesis, TU Dresden

# Stress/Texture from XRD

## 2Theta $2\theta$ / theta $\theta$ / omega $\omega$

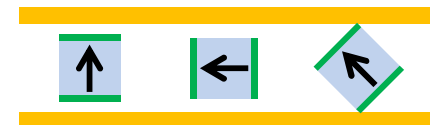
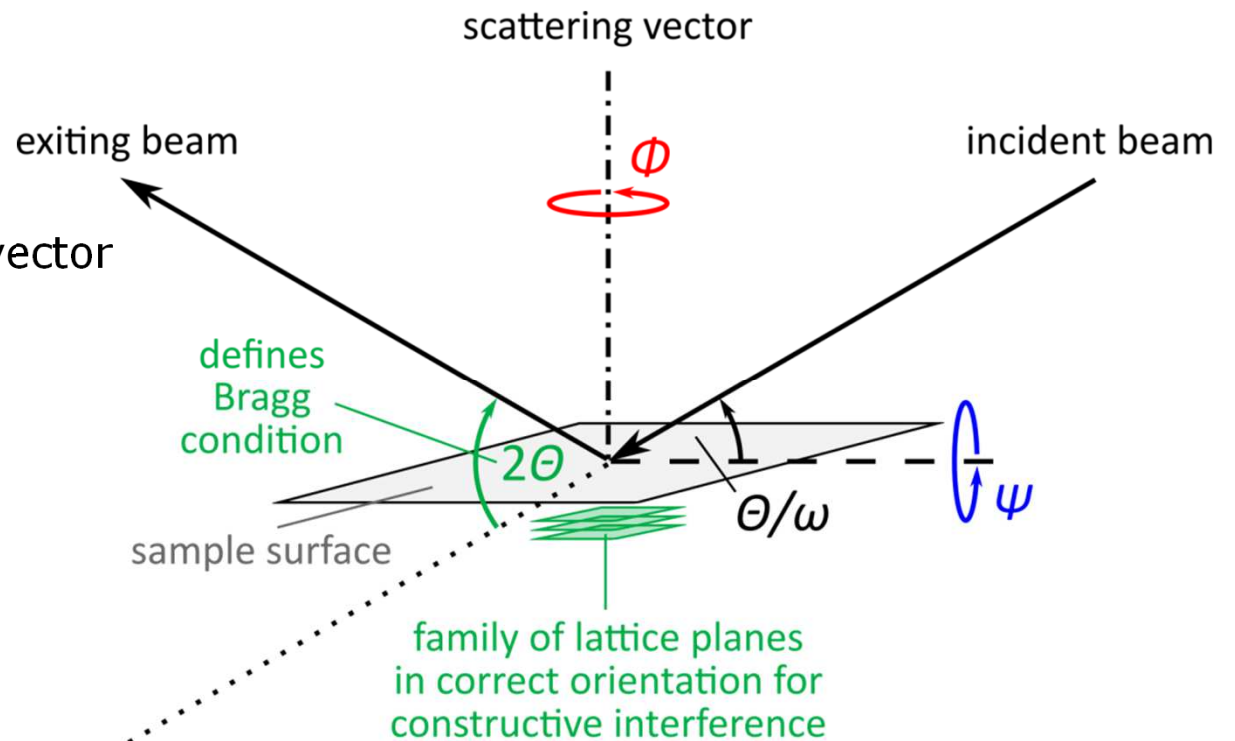
- define conditions for constructive interference in Bragg equation

→ occurrence of peaks

## Phi $\phi$

- rotation around film plane vector

→ no change of angle between scattering vector and film plane vector



T. Schenk, PhD thesis, TU Dresden

# Stress/Texture from XRD

## 2Theta $2\theta$ / theta $\theta$ / omega $\omega$

- define conditions for constructive interference in Bragg equation

→ occurrence of peaks

### Phi $\phi$

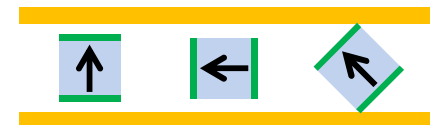
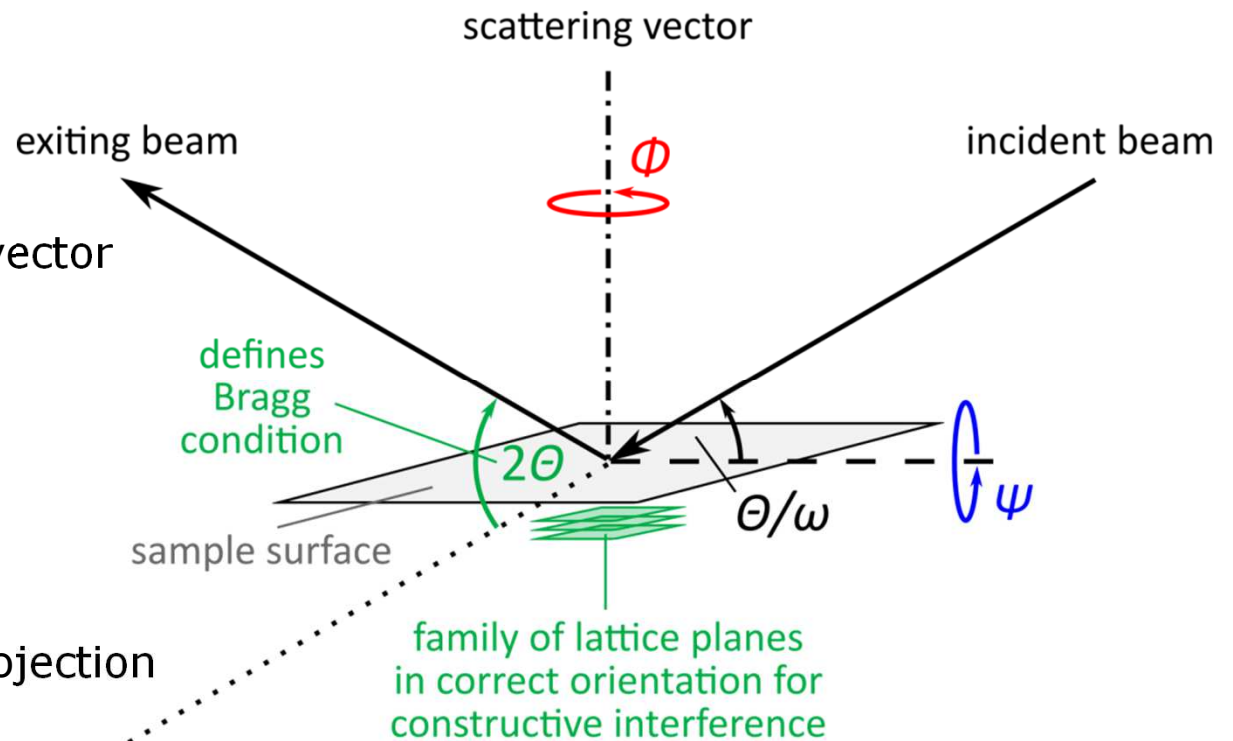
- rotation around film plane vector

→ no change of angle between scattering vector and film plane vector

### Psi $\psi$

- rotation around in-plane projection of X-ray beam

→ angle between plane vector and scattering vector



T. Schenk, PhD thesis, TU Dresden

# Stress/Texture from XRD

## Basic Formula for $\sin^2(\Psi)$ -Method

$$\varepsilon_{\Phi,\Psi} = \frac{d_{\Phi,\Psi} - d_0}{d_0} = \varepsilon_{11} \cos^2(\Phi) \sin^2(\Psi) + \varepsilon_{12} \sin(2\Phi) \sin^2(\Psi) + \varepsilon_{22} \sin^2(\Phi) \sin^2(\Psi) \\ - \varepsilon_{33} \sin^2(\Psi) + \varepsilon_{33} + \varepsilon_{13} \cos(\Phi) \sin(2\Psi) + \varepsilon_{23} \sin(\Phi) \sin(2\Psi).$$

- The following assumptions allow simplification:

→ no shear components

$$\varepsilon_{12} = \varepsilon_{13} = \varepsilon_{23} = 0$$

→ symmetric in-plane strain

$$\varepsilon_{11} = \varepsilon_{22}$$

(Check for rotation-invariant XRD patterns!)

I. C. Noyan et al., Crit. Rev. Solid State Mater. Sci. 1995, DOI: 10.1080/10408439508243733  
J. C. Nino et al., Thin Solid Films, DOI: 0.1016/j.tsf.2008.12.01

# Stress/Texture from XRD

## Simplified Formula for $\sin^2(\Psi)$ -Method

$$\varepsilon_{\Psi} = \frac{d_{\Psi} - d_0}{d_0} = [\varepsilon_{11} - \varepsilon_{33}] \sin^2(\Psi) + \varepsilon_{33}$$

→  $\varepsilon_{\Psi}$  vs.  $\sin^2(\Psi)$  plot allows extraction of in-plane  $\varepsilon_{11}$  and out-of-plane  $\varepsilon_{33}$  strain

- **Problem:** Knowledge of  $d_0$  is essential!

→ not the case for novel ferroelectrics such as  $\text{HfO}_2/\text{ZrO}_2$ .

→ generally, an issue for thin films compared to bulk materials

- **Solution:** Analysis via knowledge of elastic properties (or sufficient estimates)

I. C. Noyan et al., Crit. Rev. Solid State Mater. Sci. 1995, DOI: 10.1080/10408439508243733  
J. C. Nino et al., Thin Solid Films, DOI: 0.1016/j.tsf.2008.12.01

# Stress/Texture from XRD

## Simplified Formula for $\sin^2(\Psi)$ -Method

- Equibiaxial stress links  $\varepsilon_{11}$  and  $\varepsilon_{33}$  via Poisson ratio:

$$\varepsilon_\Psi = \frac{d_\Psi - d_0}{d_0} = [\varepsilon_{11} - \varepsilon_{33}] \sin^2(\Psi) + \varepsilon_{33}$$

$$\varepsilon_{33} = -\frac{2\nu}{1-\nu} \cdot \varepsilon_{11}$$

$$\rightarrow d_\Psi = \boxed{\frac{1+\nu}{1-\nu} \cdot \varepsilon_{11} \cdot d_0} \cdot \sin^2(\Psi) + \boxed{\left[1 - \frac{2\nu}{1-\nu} \cdot \varepsilon_{11}\right] \cdot d_0}$$

slope m                      y-intercept m

- Solutions for  $\varepsilon_{11}$  and  $d_0$  are:

$$\varepsilon_{11} = \frac{(1-\nu)m}{(1+\nu)n + 2 \cdot \nu \cdot m}$$

$$d_0 = \frac{(1+\nu)n + 2 \cdot \nu \cdot m}{1+\nu}$$

- Stress can be calculated as:

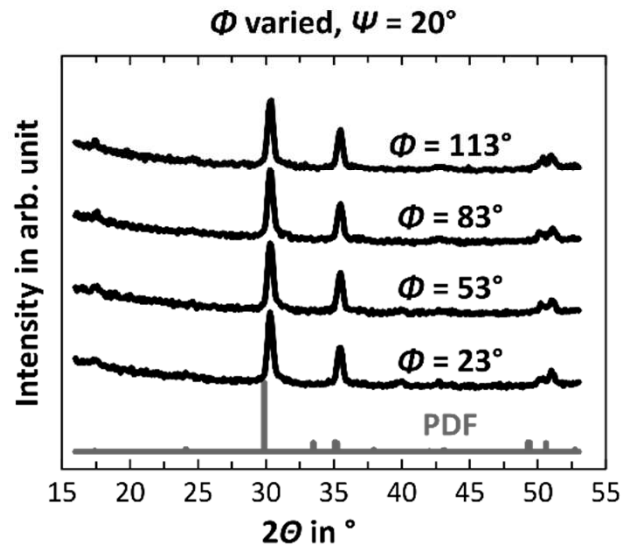
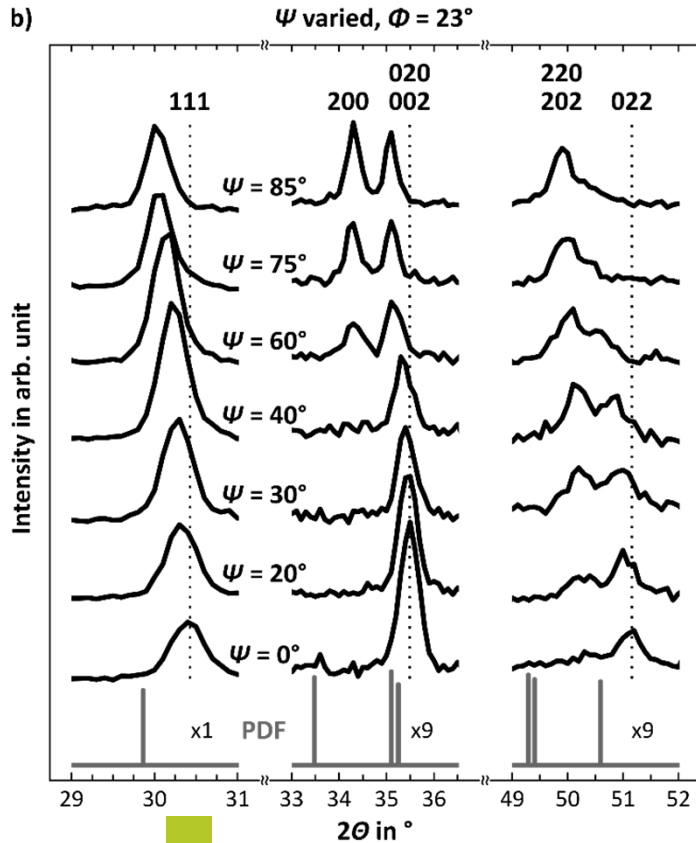
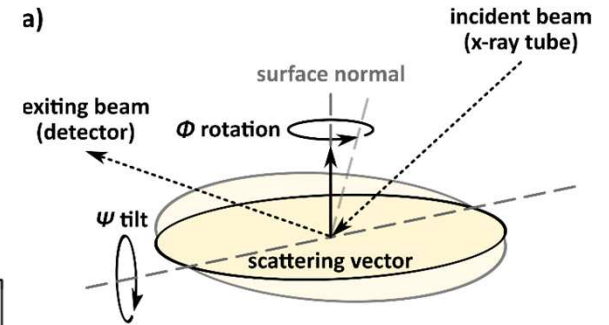
$$\sigma_{11} = \sigma_{22} = \frac{Y}{1-\nu} \cdot \varepsilon_{11}$$

$$\sigma_{33} = Y \cdot \varepsilon_{33} + 2 \cdot \nu \cdot \sigma_{11} = 0$$

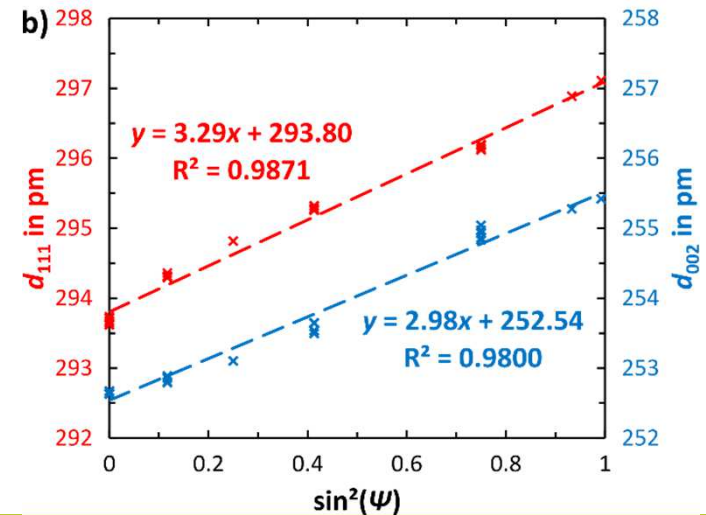
T. Schenk et al. (in review)

# Stress/Texture from XRD

20 nm La:HfO<sub>2</sub>



**Indeed, in-plane rotational symmetry!**



shift in  $2\theta$

T. Schenk et al. (in review)

# Stress/Texture from XRD

## Calculated Stress and Strain

- literature values from diff. phases for uncertainty assessment
- stress still depends directly on  $Y$
- strain only weakly dependent on  $\nu$

→ **self-consistent, more reliable approach compared to calc. based on ref. LPs**  
(LP accuracy of less than 0.1 % required)

- tensile in-plane and compressive plane-normal strain  $\approx \pm 0.5$  %
- tensile in-plane stress of  $\approx 2$  GPa

→ **extrinsic parameters; rather large values**

→ **similar to  $\text{HfO}_2$  with other dopants**

values for mono. phase:

$$Y = 284 \text{ GPa} \quad \nu = 0.3$$

S. L. Dole et al., J. Am. Cer. Soc. 1977,  
DOI: 10.1111/j.1151-2916.1977.tb14088.;

<u><math>Y</math> in GPa</u>	284	250	350	250	350
$\nu$	0.30	0.25	0.25	0.35	0.35
111 Peak ( $2\theta \approx 30.3^\circ$ )					
$d_0$ in pm	295.3	295.12		295.51	
$\epsilon_{11} = \epsilon_{22}$ in %	0.60	0.67		0.54	
$\epsilon_{33}$ in %	-0.51	-0.45		-0.58	
$\sigma_{11} = \sigma_{22}$ in GPa	2.43	2.23	3.12	2.06	2.89
$\sigma_{33}$ in GPa	0	0	0	0	0
020/002 Peak ( $2\theta \approx 35.3^\circ$ )					
$d_0$ in pm	253.9	253.73		254.1	
$\epsilon_{11} = \epsilon_{22}$ in %	0.63	0.70		0.56	
$\epsilon_{33}$ in %	-0.54	-0.47		-0.61	
$\sigma_{11} = \sigma_{22}$ in GPa	2.56	2.35	3.29	2.17	3.04
$\sigma_{33}$ in GPa	0	0	0	0	0

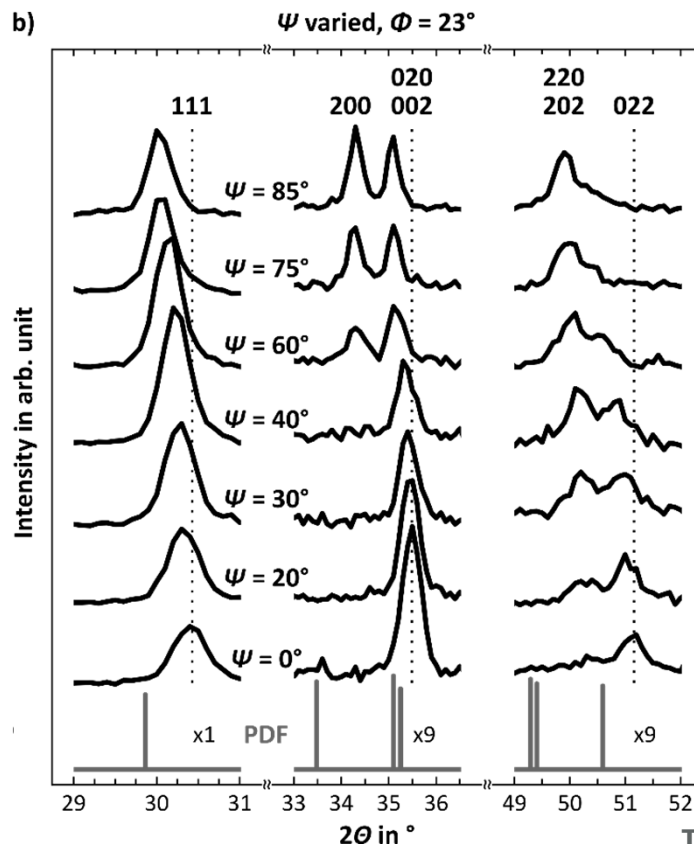
T. Schenk et al. (in review)



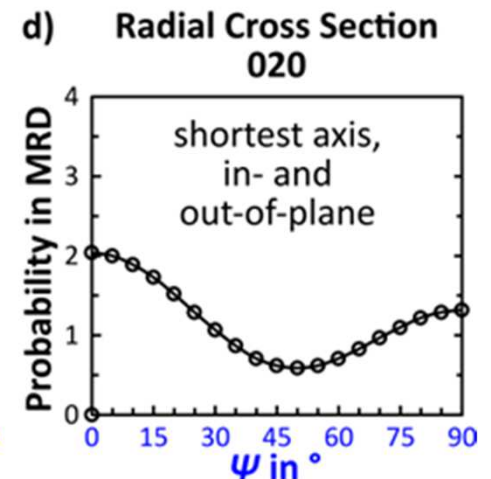
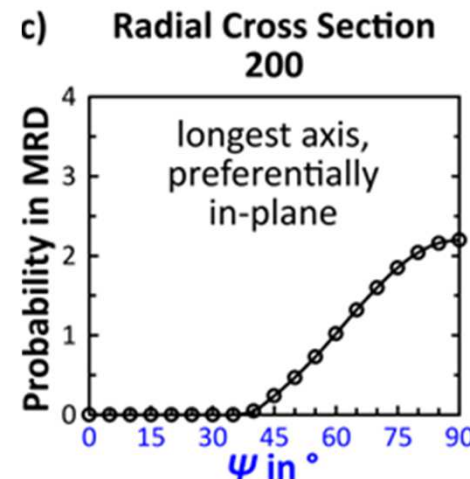
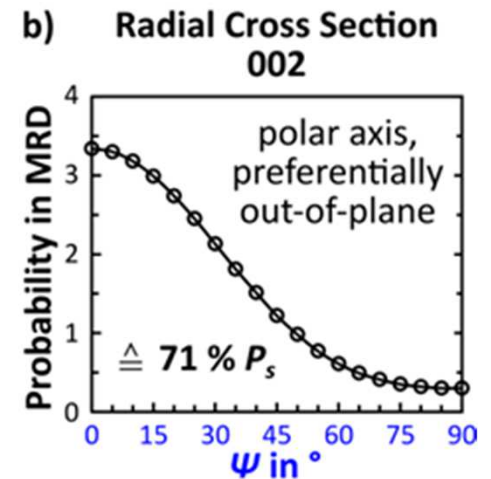
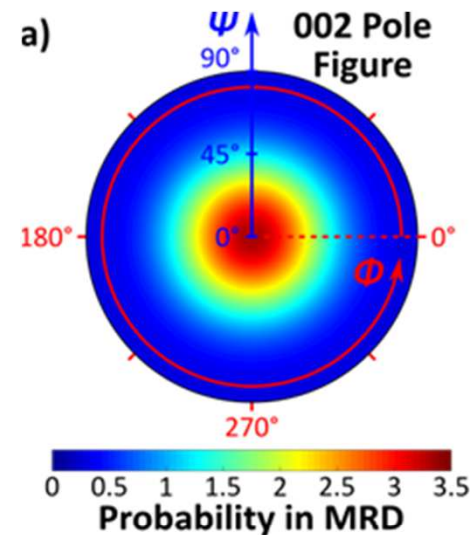
# Stress/Texture from XRD

## Preferential Orientation

- longest axis favorably in-plane
- polar axis tends to favor the plane-normal direction



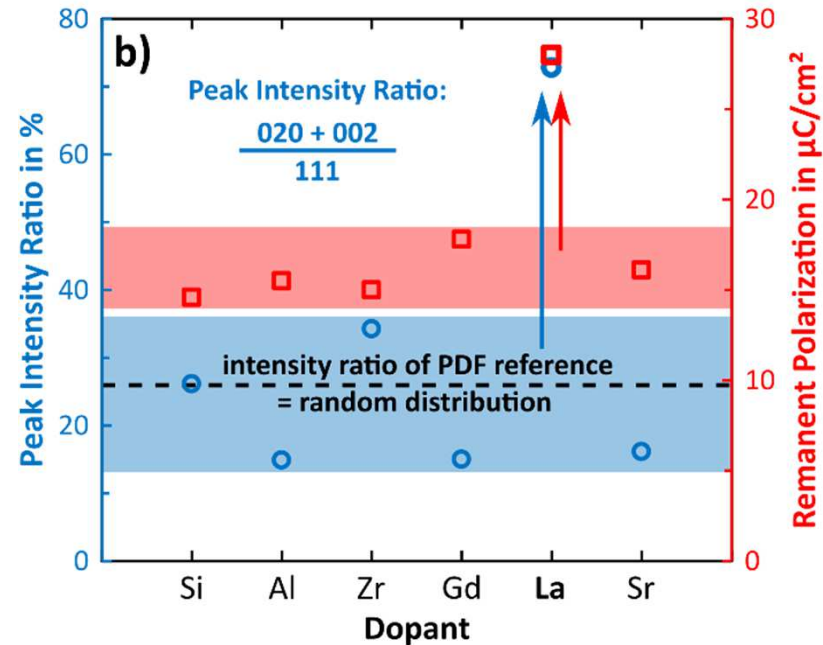
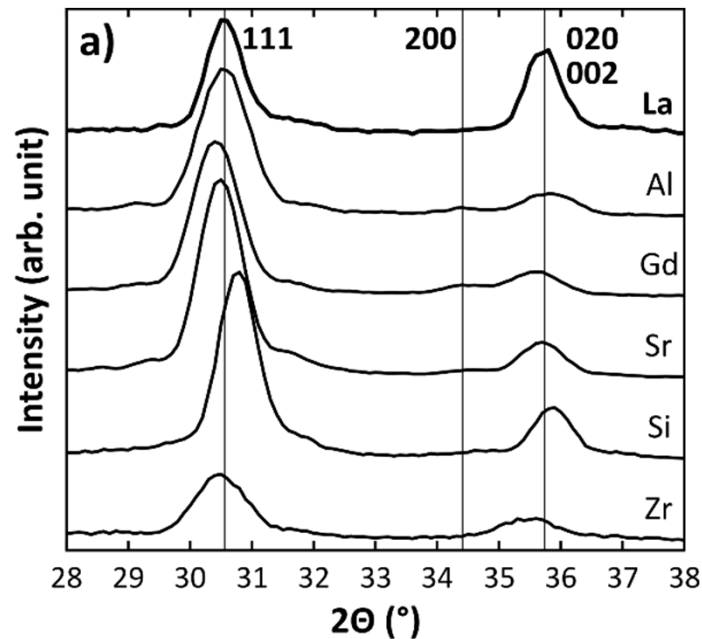
T. Schenk et al. (in review)



# Stress/Texture from XRD

## Relation of Texture and $P_r$

- Already in GIXRD, La:HfO<sub>2</sub> is indeed a bit special.



→ Watch out for such features!

- random orientation → max.  $P_r$  = 50 % of  $P_s$
- integrated pole figure → max.  $P_r$  = 58 % of  $P_s$

T. Schenk et al. (in review)

# Outline

Introduction

Basic Experimental Data & Theory

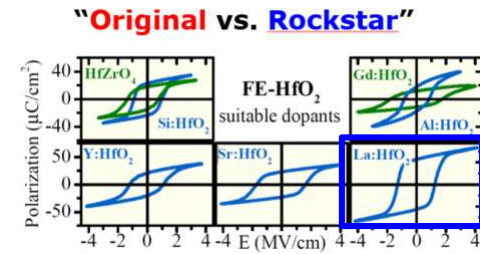
Stress/Texture from XRD

Summary and Outlook

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## “Rockstar” La:HfO<sub>2</sub>

- reports on large  $P_r$  and wide dopant conc. window



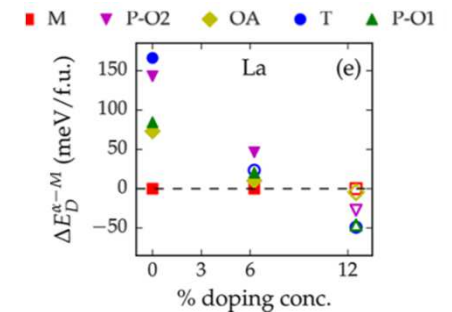
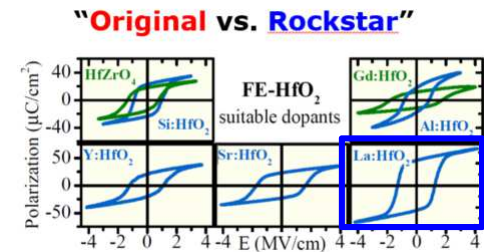
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- La is a strong stabilizer of the polar phase
- La leads to 62  $\mu\text{C}/\text{cm}^2$ , others: 50 - 60  $\mu\text{C}/\text{cm}^2$



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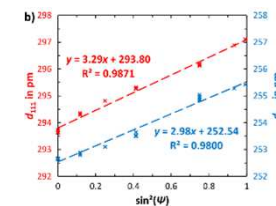
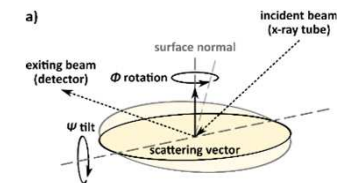
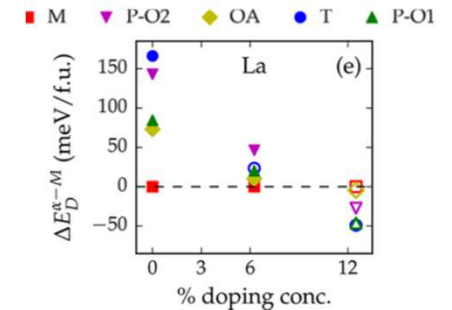
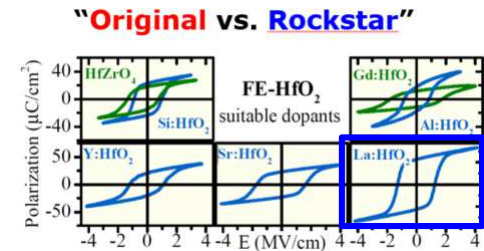
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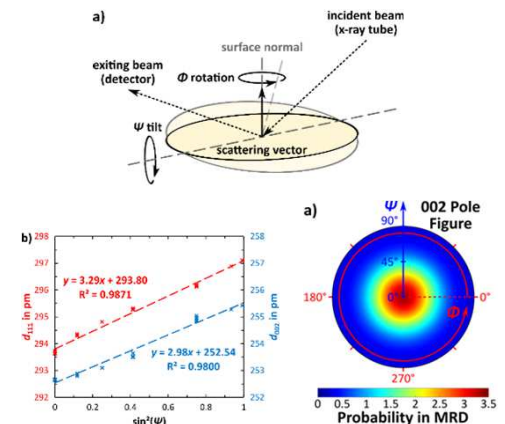
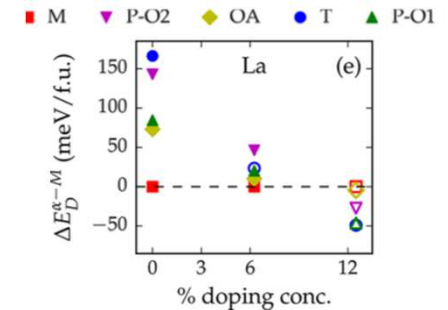
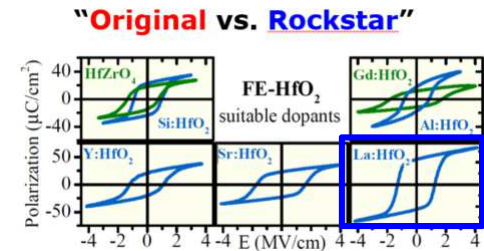
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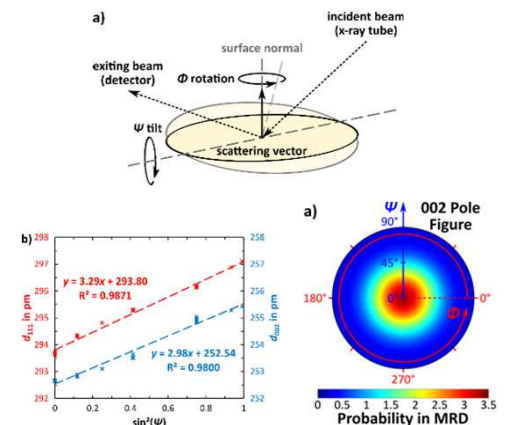
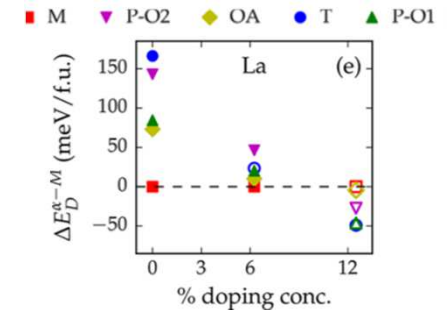
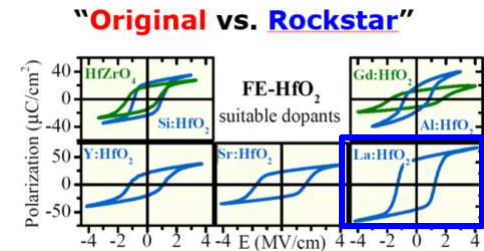
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**Future work:** Why does texture develop differently in La:HfO<sub>2</sub>?

→ Interplay of large FE phase fraction and stress?; Kinetic effect during anneal?





EuroCVD 22 Baltic ALD 16 | 2019  
24-28.06.2019 | Luxembourg



# Thanks for your kind attention!

## Thanks to the organizers!

### Acknowledgements:

My collaborators from:



PUSAN  
NATIONAL UNIVERSITY



The German Research Foundation (DFG) and the Fonds National de la Recherche Luxembourg (FNR) are acknowledged for funding parts of this work in the projects "Inferox" (project no. MI 1247/11-2) and CO-FERMAT (FNR/P12/4853155/Kreisel), respectively.

# Introduction

## Rietveld Refinement

	tetragonal phase refined	orthorhombic phase refined	$\sin^2(\psi)$ -approach
$a$ in Å	3.5914(3)	5.207(1)	5.20
$b$ in Å	3.5914(3)	5.073(1)	5.07
$c$ in Å	5.2038(11)	5.086(1)	5.08
$\sigma_{11} = \sigma_{22}$ in GPa	2.24(4)	2.17(4)	2.43/2.56

- low-index peaks (100, 110 and so on) distinguish orth. from tetra. phase

