

# 铁电物理研究新进展

## New Progress in Ferroelectrics

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细推物理须行乐

何用浮名绊此生

杜甫

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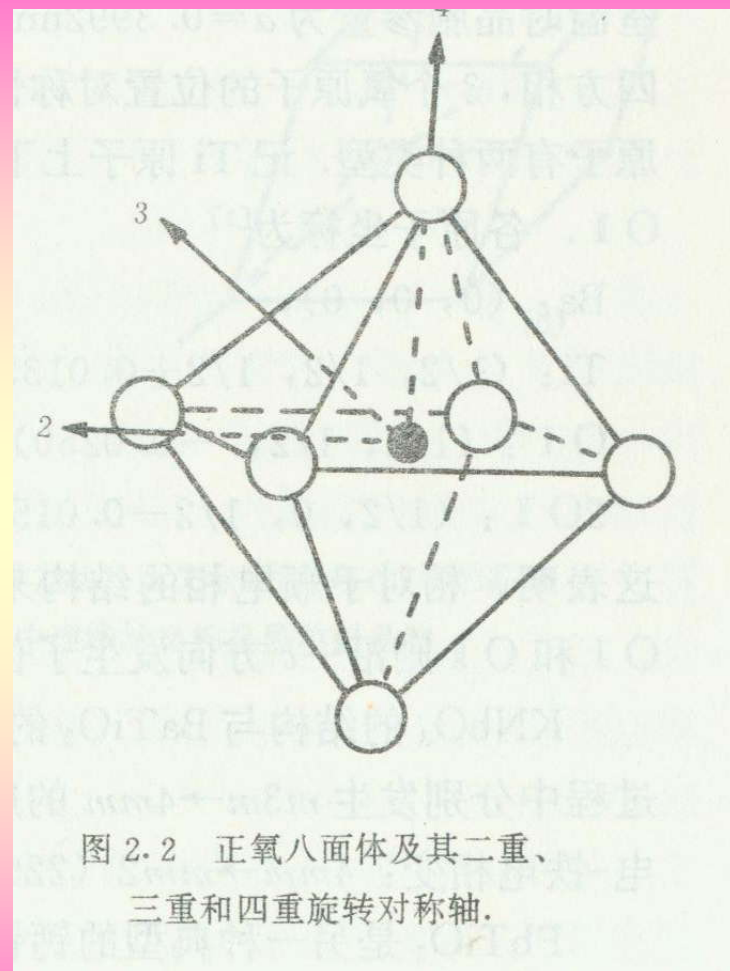
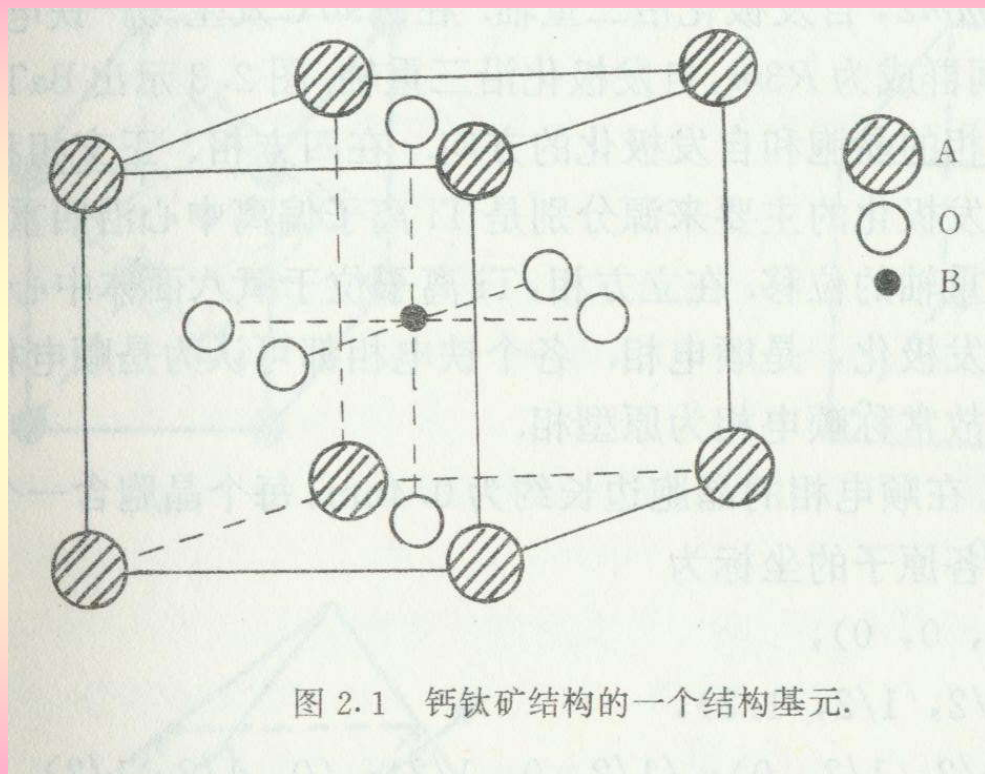
# 1. History of Ferroelectrics (Ferromagnetics)

@166 (5) 5年前后 法国La Rochelled地方人  
Pierre de la Seignette最早试制成功罗息盐 (RS)  
(酒石酸甲钠,  $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ )  
Sodium Potassium Tartrate Tetrahydrate

@1920年 法国人Valasek发现罗息盐的 特异的  
非线性介电性能, 导致了“铁电性”概念的出现.  
1920年成为铁电物理学研究开始的象征?

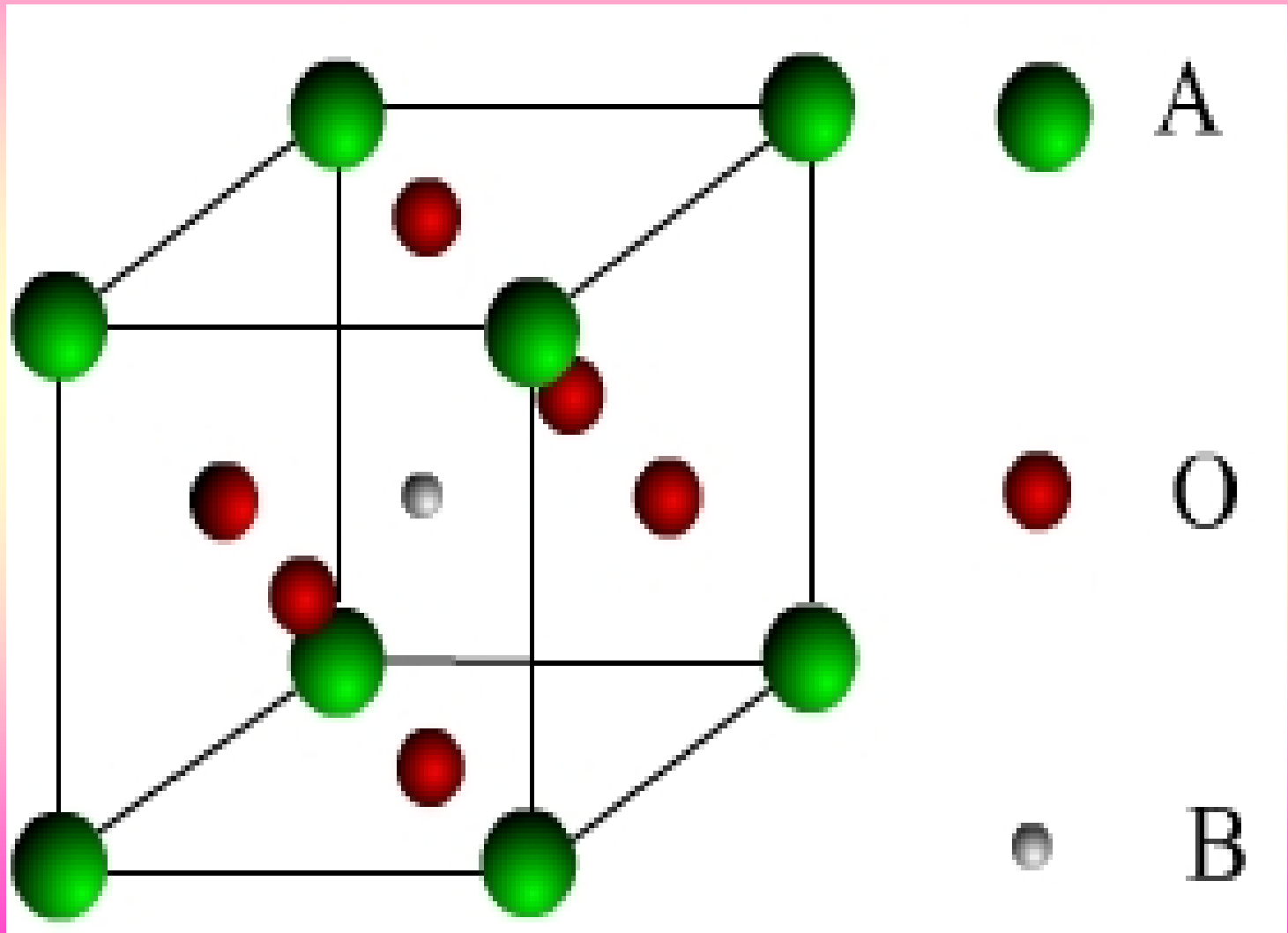
目前, 世界上存在200多种铁电体

铁电体的晶体结构:  $ABO_3$  ( $ABF_3$ ) perovskite structure  
with  $A^{2+}B^{4+}$  or  $A^{1+}B^{5+}$   
octahedra



钙钛矿( $ABO_3$ ) 型铁电体是为数最多的一类铁电体

# 钙钛矿结构的一个结构单元



## **Pierre Curie**

was born in Paris,  
on May 15, 1859.

Pierre was killed  
in a street accident  
in Paris  
on April 19, 1906



# Marie Curie

*Born in Warsaw on  
November 7, 1867*

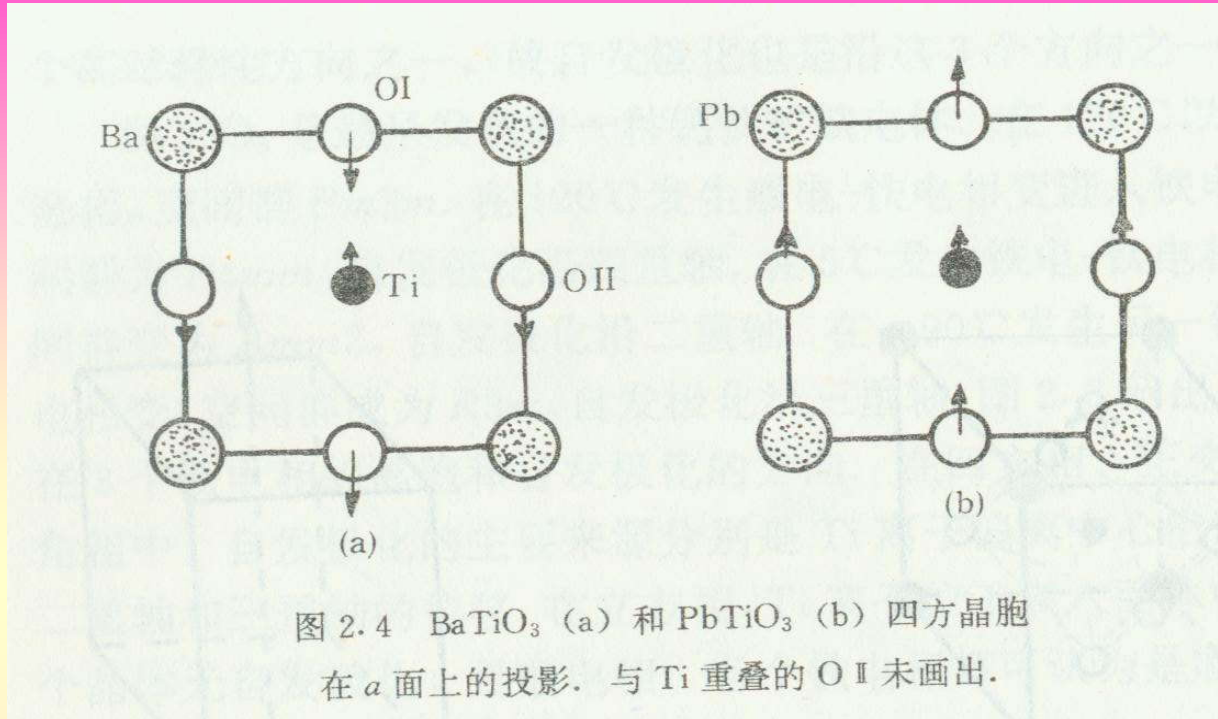


**Marie died of  
leukaemia in  
July, 1934**

*A Nobel Prize Pioneer at the Panthéon*

**The ashes of Marie Curie and her husband Pierre have now been laid to rest under the famous dome of the Panthéon, in Paris, alongside the author Victor Hugo, the politician Jean Jaurès and the Resistance fighter Jean Moulin. Through her discovery of radium, Marie Curie paved the way for nuclear physics and cancer therapy. Born of Polish parents, she was a woman of science and courage, compassionate yet stubbornly determined. Her research work was to cost her her life.**

# 自发极化的产生



顺电相: Ba:  $(0, 0, 0)$       Ti:  $(1/2, 1/2, 1/2)$ ,  
 3O:  $(1/2, 1/2, 0)$ ;  $(1/2, 0, 1/2)$ ;  $(0, 1/2, 1/2)$

铁电相: Ba:  $(0, 0, 0)$       Ti:  $(1/2, 1/2, 1/2+0.0135)$ ,  
 O I:  $(1/2, 1/2, -0.0250)$ ,  
 2O II:  $(1/2, 0, 1/2-0.0150)$ ;  $(0, 1/2, 1/2-0.0150)$



# 重要特征：铁电体的电滞回线 (hysteresis loop)

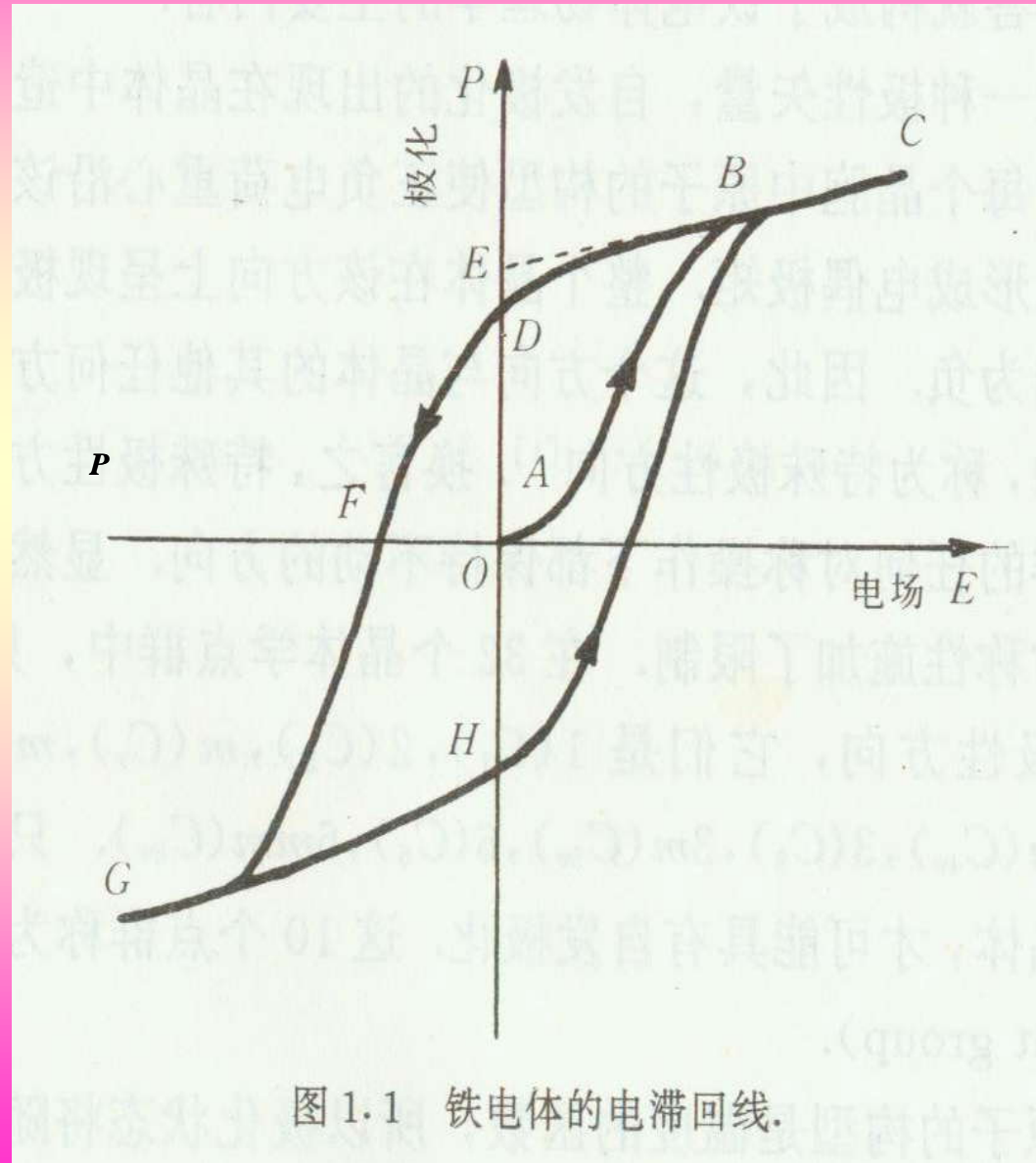
OD:  $P_r$   
remanent polarization

OE:  $P_s$   
spontaneous polarization

OF:  $E_c$   
coercive field

E: electric field

P: polarization amplitude



## 2. 研究内容: **bulk materials** $\longrightarrow$ **thin films**

@核心问题 自发极化 spontaneous polarization

@自发极化是怎样产生的?

@自发极化与晶体结构和电子结构有什么关系?

@在各种外界条件作用下极化状态怎样变化?

@特殊的物理性质和应用

## 五个研究阶段：

第一阶段（1920—1939年）

两种铁电结构材料，即罗息盐和 $\text{KH}_2\text{PO}_4$ 系列；

第二阶段（1940—1958年）

Landau铁电唯象phenomenological理论开始建立，并趋于成熟；

第三阶段（1959—70年代）

铁电软模(Soft-Mode)理论出现和基本完善；

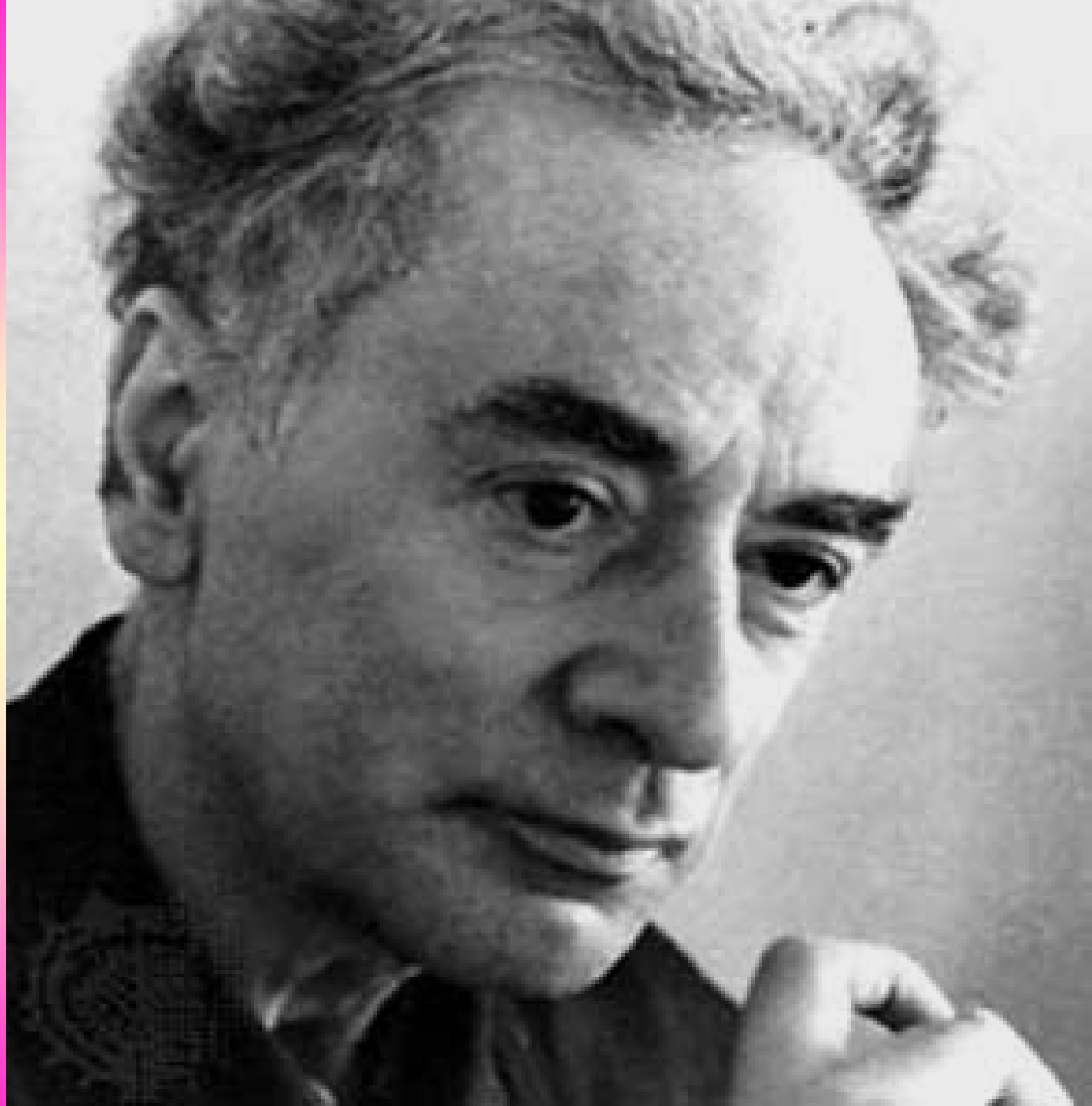
第四阶段（80年代至今）

主要研究各种非均匀系统。

第五个阶段：96年开始铁电薄膜和铁电薄膜器件

# **Lev Davidovich Landau**

**Born: 22 Jan 1908  
in Baku,  
Azerbaijan,  
Russian Empire  
Died: 1 April 1968  
in Moscow,  
USSR**



# Several Important Concepts:

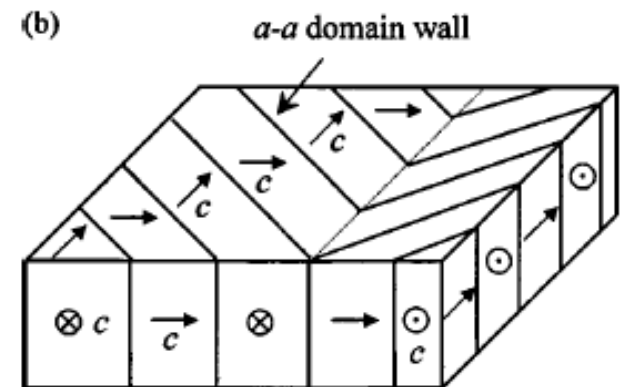
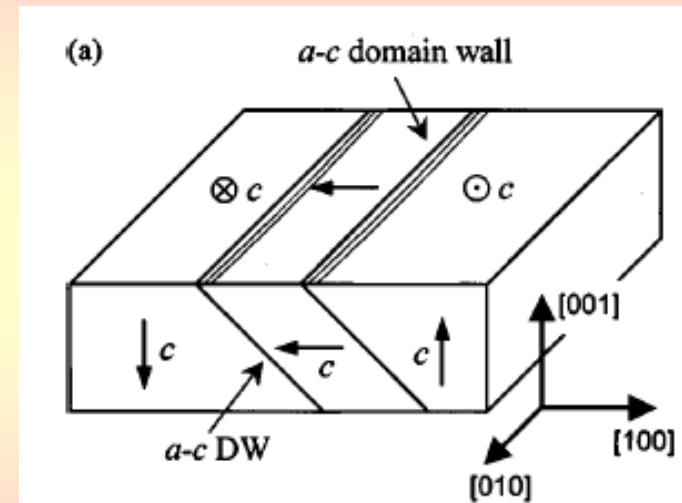
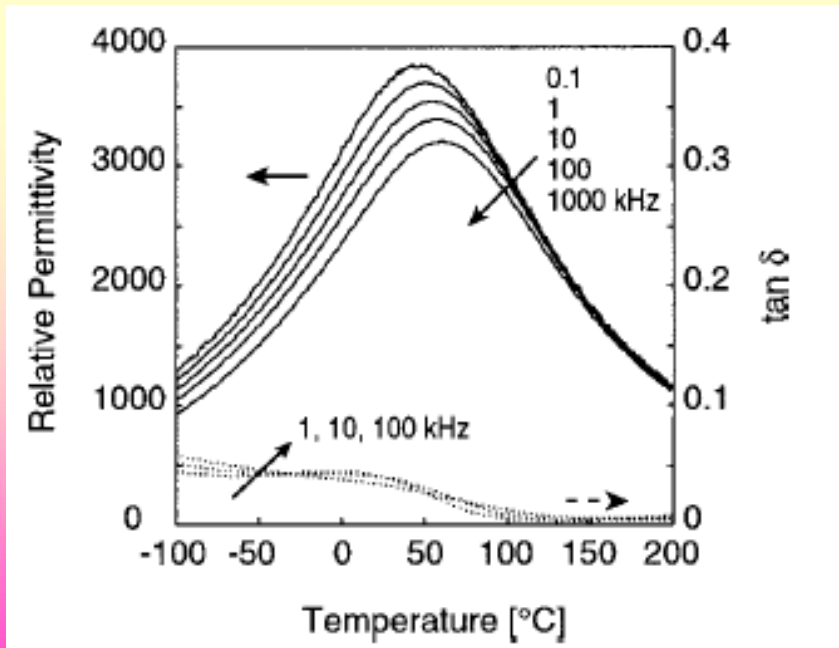
@铁电相变: phase transition of ferroelectrics

@铁电相与顺电(paraelectricity)相之间的转变

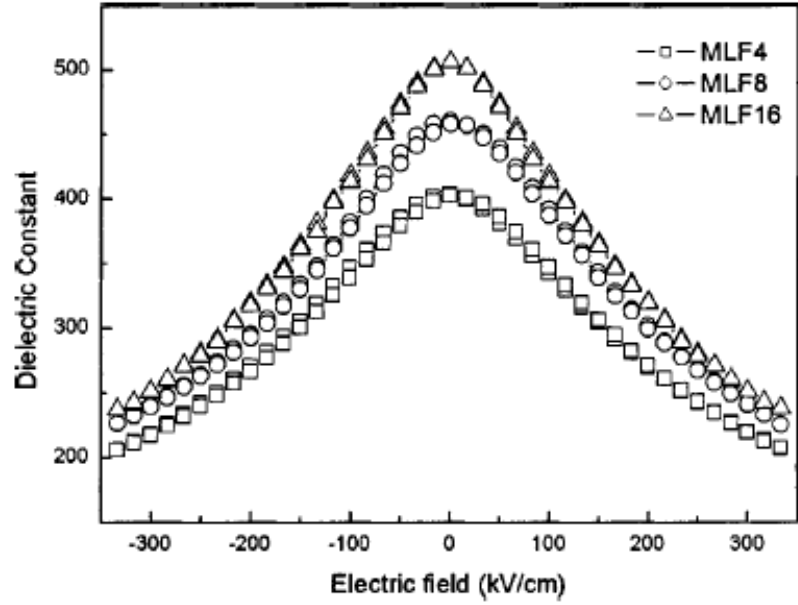
@居里温度(居里点)  $T_c$  铁电体(ferroelectric)

变成顺电体(paraelectric)

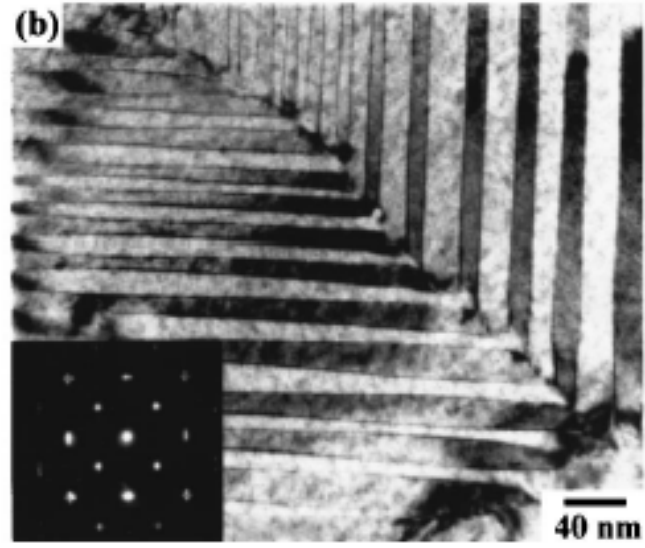
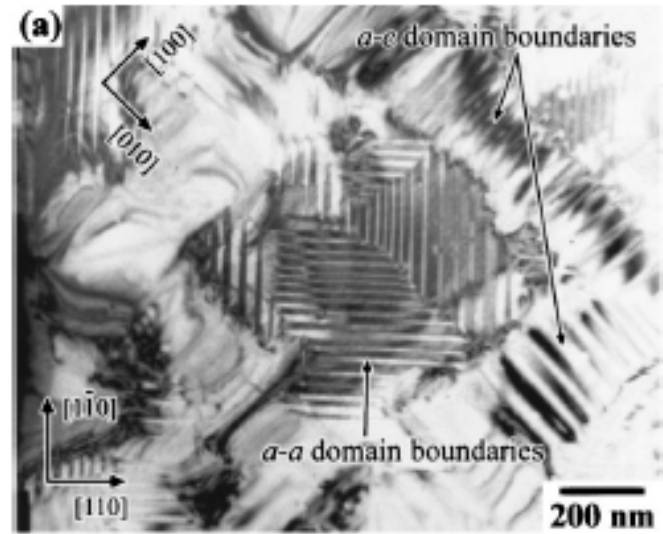
@实质: 自发极化出现或消失

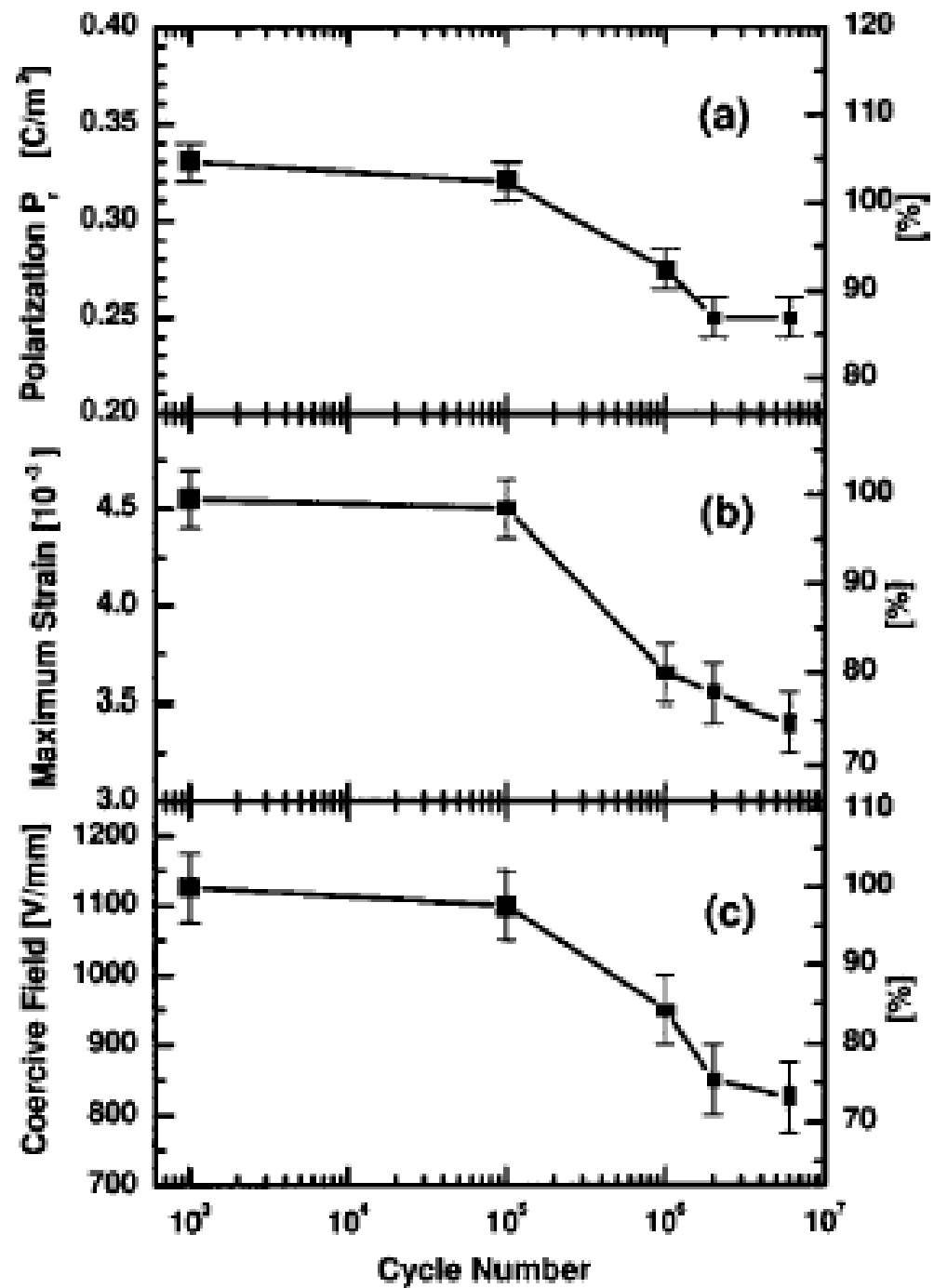


# Domain and Domain Wall



## Dielectric Constant





### 3.铁电理论I：铁电宏观理论--朗道相变理论

将对称破缺引入到相变理论，强调对称性的重要性，对称性的存在与否是不容模棱两可的，高对称性相中某一对称元素突然消失，就对应于相变的发生，导致低对称相的出现。

对称性

有序化程度

**序参量：**描写系统内部有序化程度，表征相变过程的基本参量.高对称相中为零，低对称相中不为零.序参量和对称破缺对温度的依赖性



# Landau理论的具体表达:

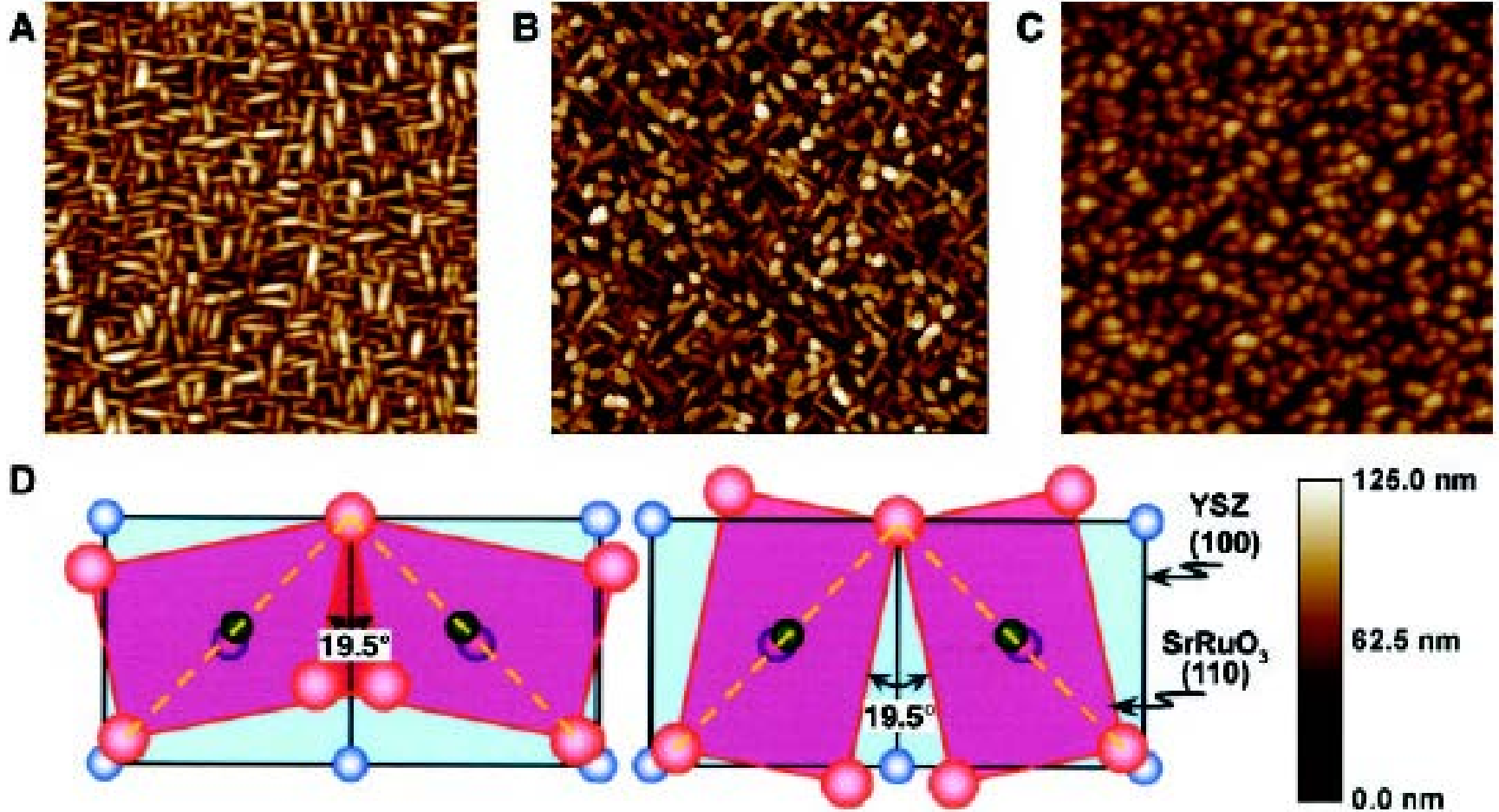
自由能作为序参量的函数。

序参量：标量、矢量、张量或复数。

在相变点附近，将自由能展开：

$$F(T, \eta) = F_0(T) + \alpha_2(T)\eta^2 + \alpha_4(T)\eta^4 + \dots$$

# Ferroelectric $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$



$$F(T, \eta) = F_0(T) + \alpha_2(T)\eta^2 + \alpha_4(T)\eta^4 + \dots$$

$T' > T_c$      $\eta = 0$  使自由能达到极小     $\alpha_2(T') > 0$

$T'' < T_c$      $\eta \neq 0$  使自由能达到极小     $\alpha_2(T'') < 0$

$\alpha_2(T') \rightarrow \alpha_2(T'')$  连续变化要求,     $\alpha_2(T_c) = 0$

$$\alpha_2(T) = \alpha_0 \bullet (T - T_c) \quad \alpha_0 > 0$$

Some important quantities can be obtained by :

序参量(order parameter):  $\partial F / \partial \eta = 0$

熵(entropy):  $S = - \left( \frac{\partial G}{\partial T} \right)$

比热(specific heat):  $C = T \frac{\partial S}{\partial T}$

特征函数：

弹性吉布斯自由能G

$$dG = -SdT - x dX + E dD$$

如果特征函数连续但一级导数不连续则相变是一级的，如果一级导数连续，但二级导数不连续，则相变是二级的。

将特征函数写为D的各偶次幂之和：

$$G = G_0 + \frac{1}{2} \alpha_0 (T - T_0) D^2 + \frac{1}{4} \beta D^4 + \frac{1}{6} \gamma D^6$$

$T_0$ : Curie-Weiss Temperature

# 铁电理论II：铁电相变的微观理论

从原子或分子机制来说明铁电体的铁电性质

根据晶体结构测定和理论分析，可将铁电相变分为两种类型：

(1)位移型: **displacive** 由于原子的非谐振动，其平衡位置相对于顺电相发生了偏移

(2)有序无序型: **order-disorder** 多个平衡位置 顺电相原子或原子团在这些位置的分布是无序的，在铁电相它们的分布有序化 ( $\text{KH}_2\text{PO}_4$ )

**$\text{BaTiO}_3$**  兼具两者特征

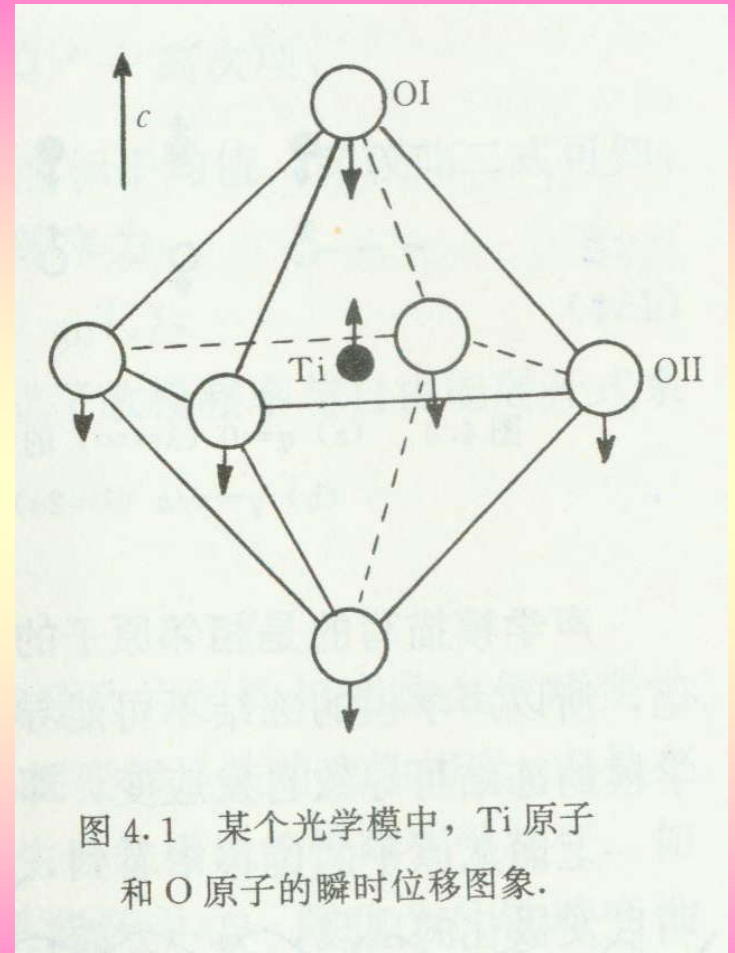
# 软模理论（位移型）：

自发极化的出现联系于布里渊区中心某个光学横模的“软化”静态位移

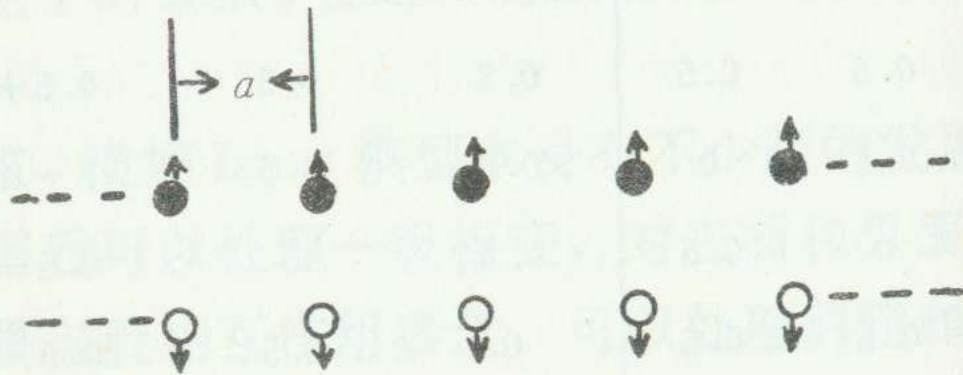
集中注意对相变负责的晶胞中少数离子单势阱中的非谐振子

软模的机制：

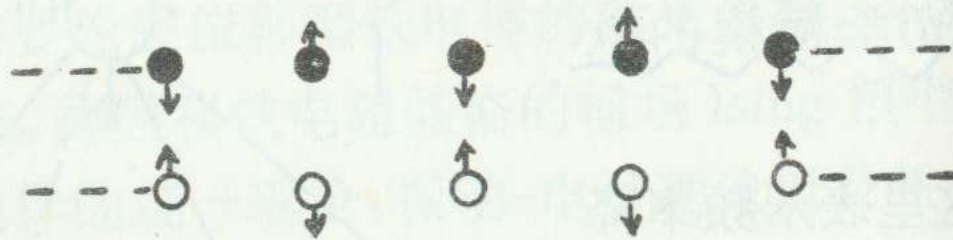
短程排斥力和长程库仑力平衡







(a)



(b)

图 4.2 (a)  $q=0$  ( $\lambda=\infty$ ) 的光学横模示意图,  $a$  为晶格常数;  
 (b)  $q=\pi/a$  ( $\lambda=2a$ ) 的光学横模示意图.

# 软模理论

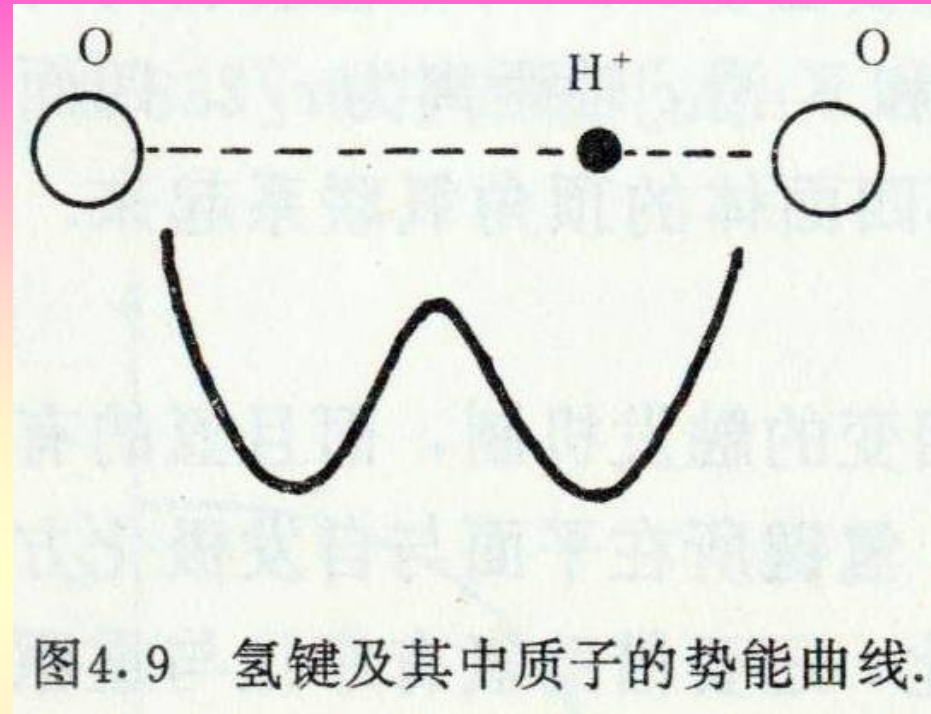
(有序无序型) :

离子在双势阱中的运动  
序参量: 氢的有序化程度

二能级系统: 对称 反对称  
隧穿频率

横场Ising模型

$$H\{s\} = -k \sum_{i \neq j} s_i s_j - h \sum_{i=1}^N s_i$$



# 微观理论的进一步发展:

软模理论:

位移型系统      晶格振动光学横模

有序无序系统      赝自旋波 (粒子在双势阱中的运动)

铁电相变的统一理论

振动-电子理论

$$E_{loc} = E + \frac{p}{3\epsilon_0} = \frac{(\epsilon + 2\epsilon_0)E}{3\epsilon_0}$$

**极化方式**：不同晶格类型中局部电场与外加电场之间的关系有几种不同的类型，但仍是争论激烈至尽未解决的问题。 “莫索蒂灾难”

(1) 克劳修斯-莫索蒂-洛伦兹模型

(2) 昂萨格模型 “空间电荷” space charge  
《电介质材料及介电性能》P107

束缚电荷 退极化场 静电能 机械约束  
应变、应力能 极化均匀程度与不稳定

电畴domain 畴壁能domain wall

总自由能取极小值的条件决定了电畴的稳定构型

# 极化反转的基本过程:

1. 新畴成核

2. 畴的纵向长大

3. 畴的横向扩张

4. 畴的合并

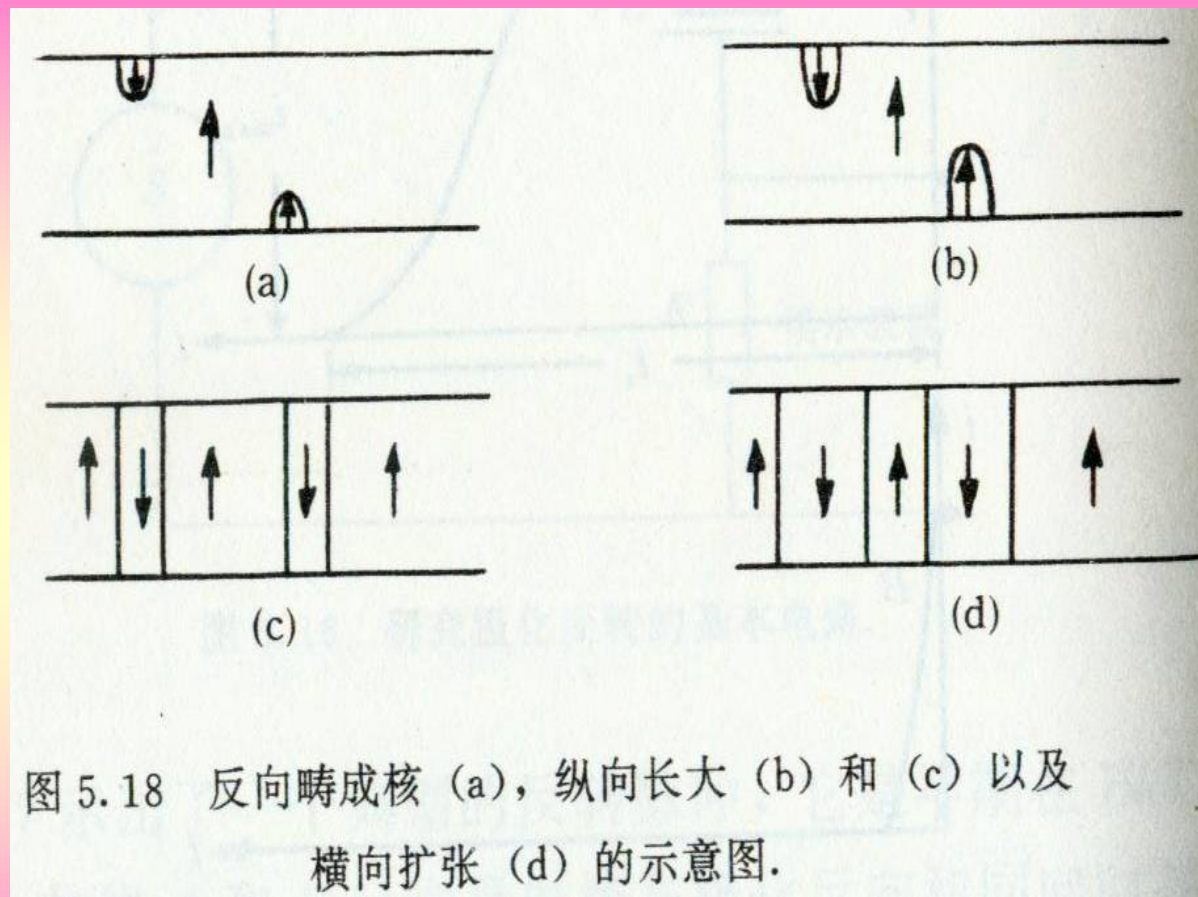


图 5.18 反向畴成核 (a), 纵向长大 (b) 和 (c) 以及横向扩张 (d) 的示意图.

# 介电响应： Dielectric Response

电介质的本质特征：以极化的方式传递、存储、或记录电场的作用和影响

基本参量：极化率（电容率 permittivity）

铁电体电容率的特点：数值大、非线性效应强、显著的温度和频率依赖性

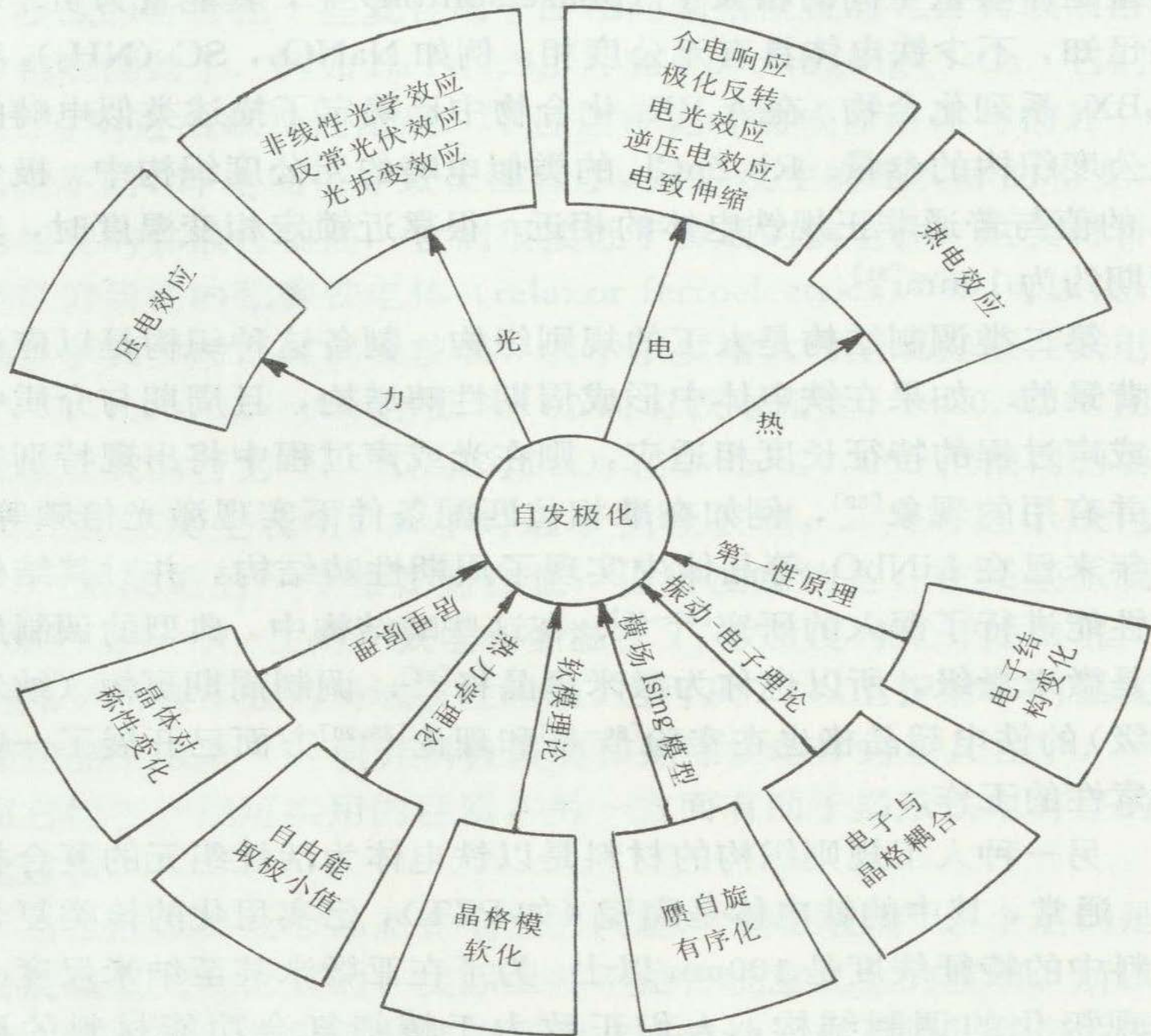
铁电体结构 缺陷 相变

## 铁电体的几个功能效应：

压电效应：在某些晶体的特定方向施加压力，相应的表面上出现正或负的电荷，而且电荷密度与压力大小成正比。

热电效应：极化随温度改变的现象

非线性光学效应、电光效应、光折变效应等





## 5. 铁电物理学研究的新进展：

### (1) 第一性原理的计算

$\text{BaTiO}_3$ 和 $\text{PbTiO}_3$ 都有铁电性，晶体结构和化学方面都与它们相同的 $\text{SrTiO}_3$ 却没有铁电性？

### (2) 尺寸效应的研究

自发极化、相变温度和介电极化率等随尺寸变化的规律，铁电体的铁电临界尺寸

- (3) 铁电液晶和铁电聚合物的基础和应用研究  
手性分子组成的倾斜的层状C相（SC\*相）液晶具有铁电性。铁电液晶在电光显示和非线性光学方面有很大吸引力。
- (4) 集成铁电体的研究：铁电薄膜与半导体的集成  
铁电随机存取存储器（FRAM）  
铁电场效应晶体管（FFET）  
铁电动态随机存取存储器（FDRAM）  
红外探测与成像器件  
超声与声表面波器件以及光电子器件等  
铁电薄膜传感器  
弛豫型铁电传感器

# Pulsed Laser Deposition (PLD)

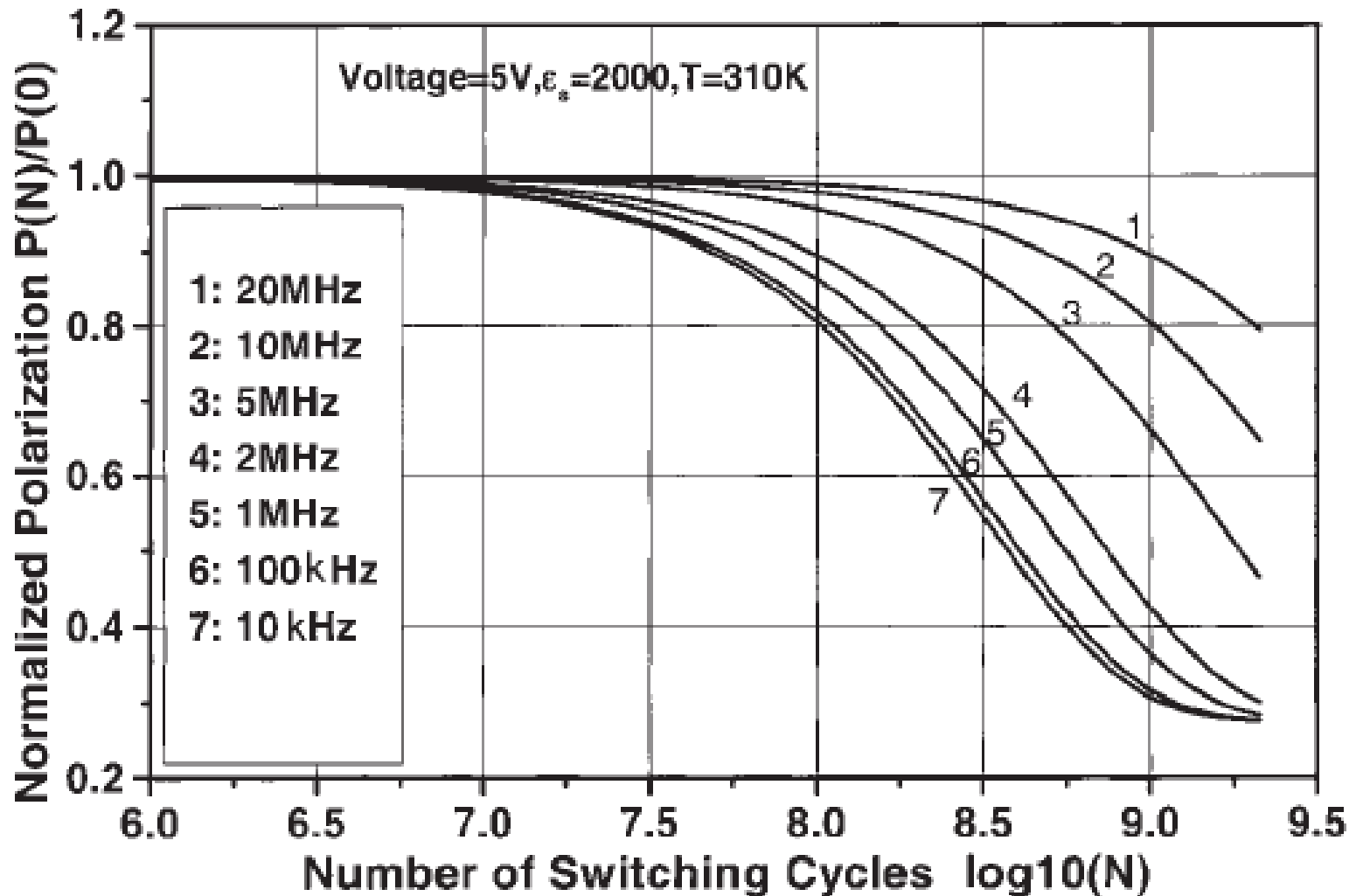


2021/11/4 Thursday

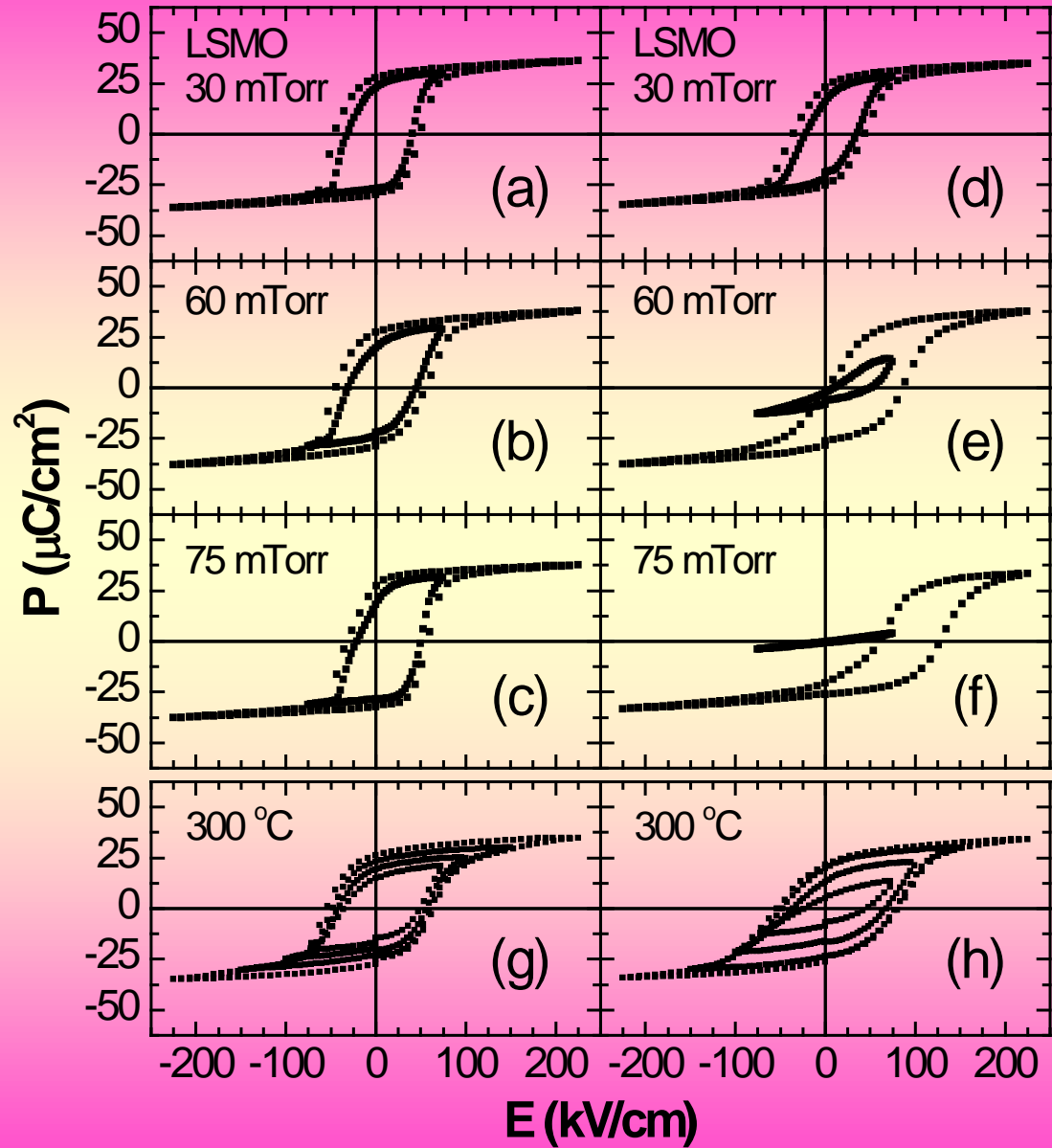


2021/11/4 Thursda

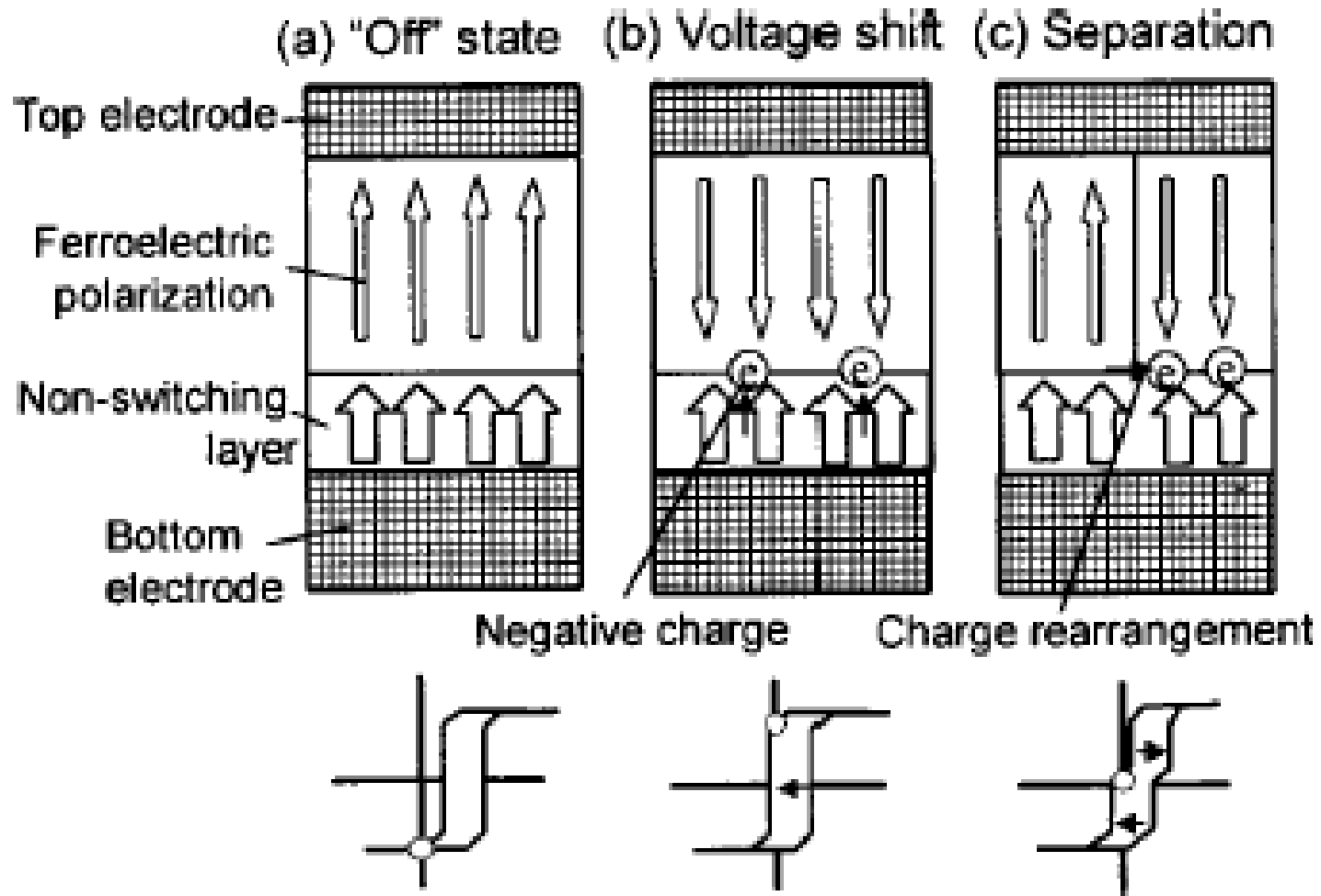
# Problems: 1) Fatigue

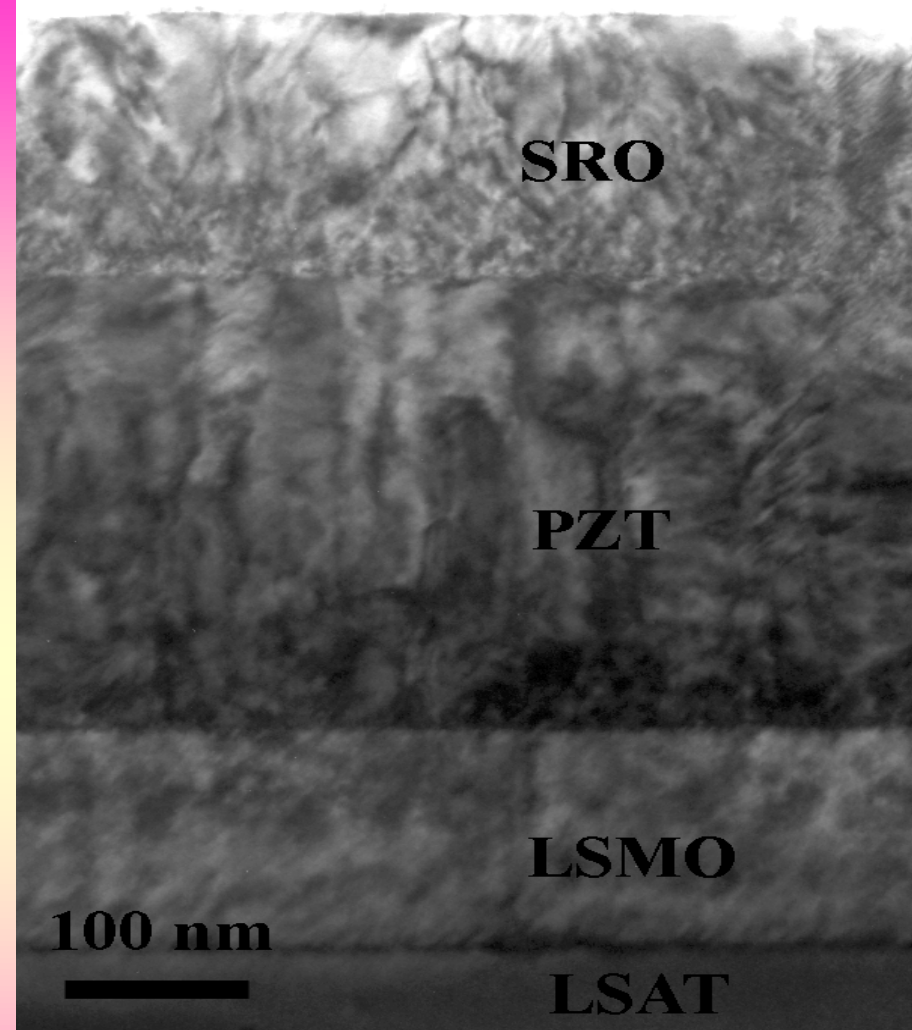


# 2) Imprint Effect



# Voltage shift phenomena





oxygen annealed (10 Torr)

2021/11/4 Thursday

— Surface layer

— Ferroelectric

⊕  
⊖ Polarization charges

+  
- Screening charges

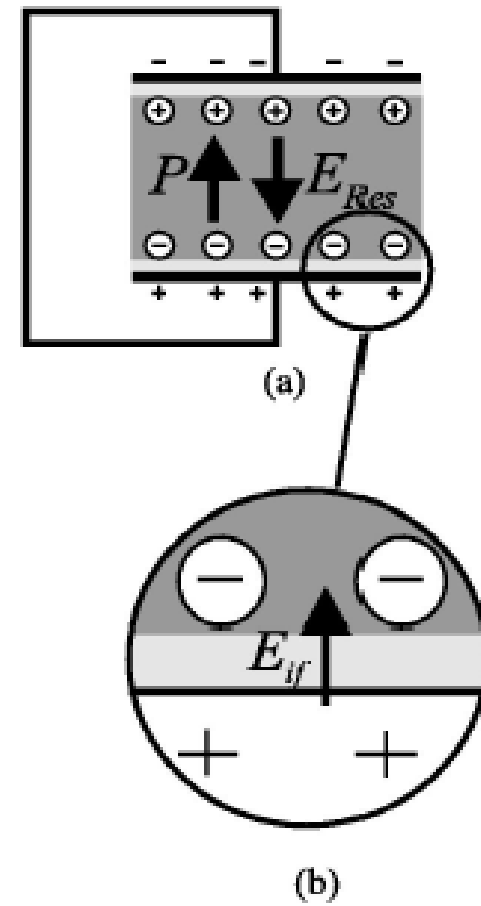
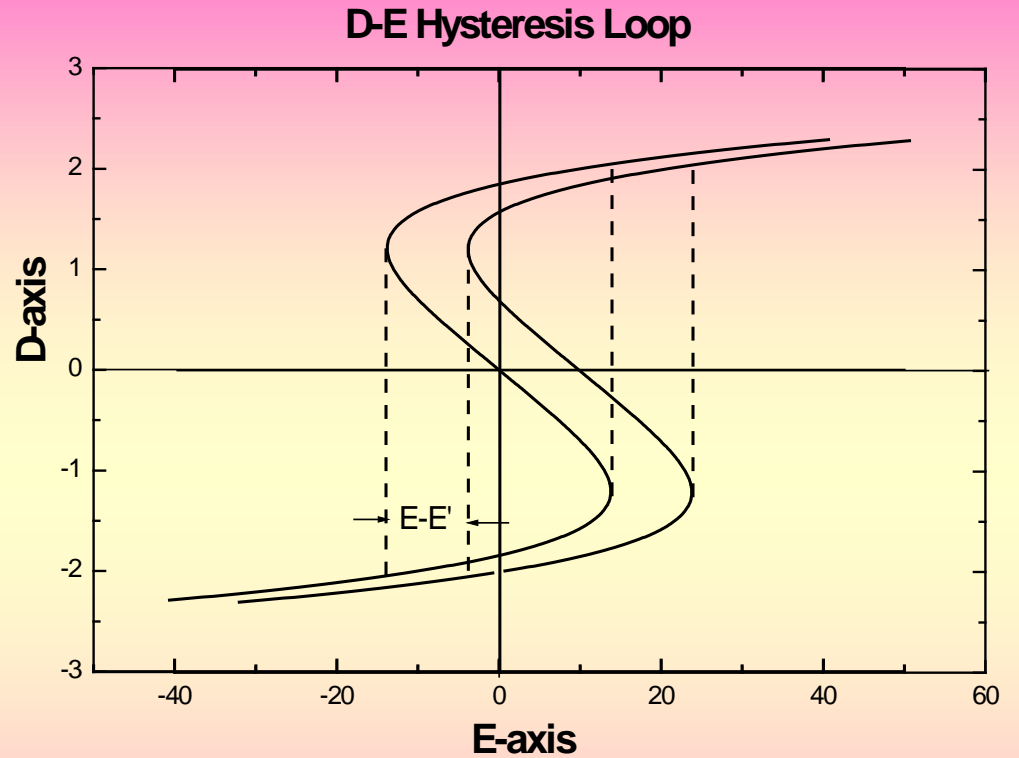
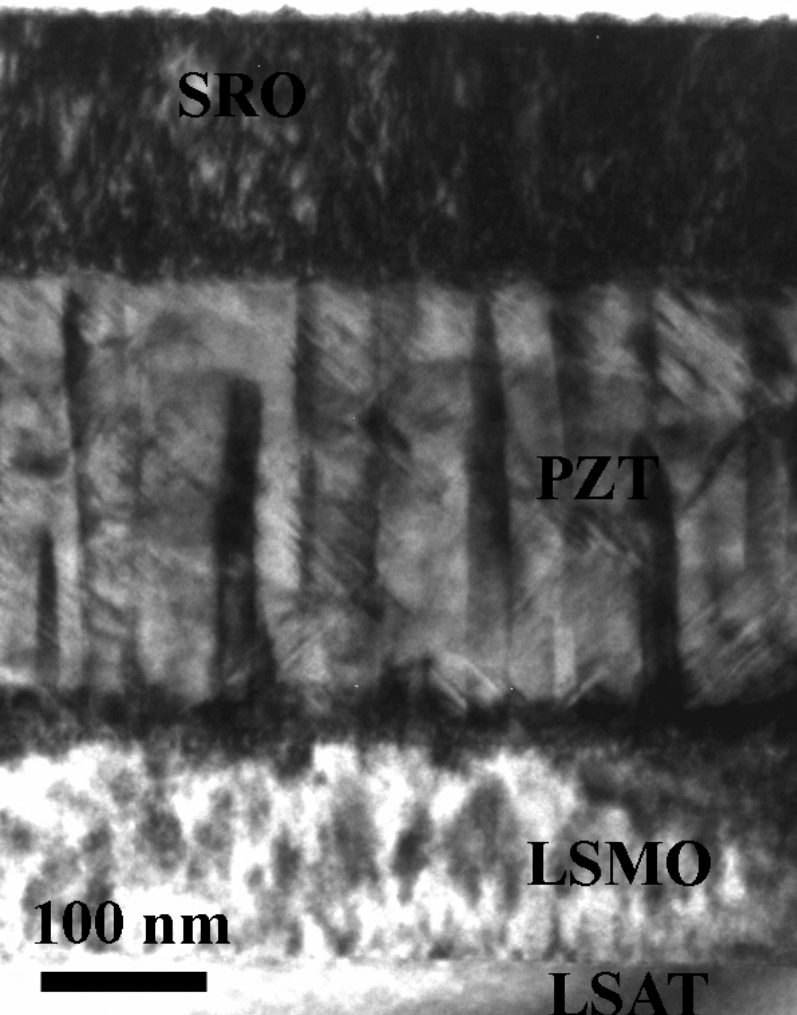


FIG. 7. (a) Sketch of the bulk screening model with the driving force  $E_{Res}$ . (b) Interface screening model: enlargement of the interfacial region showing the driving force of the interface screening model,  $E_{if}$ , in the surface layer.



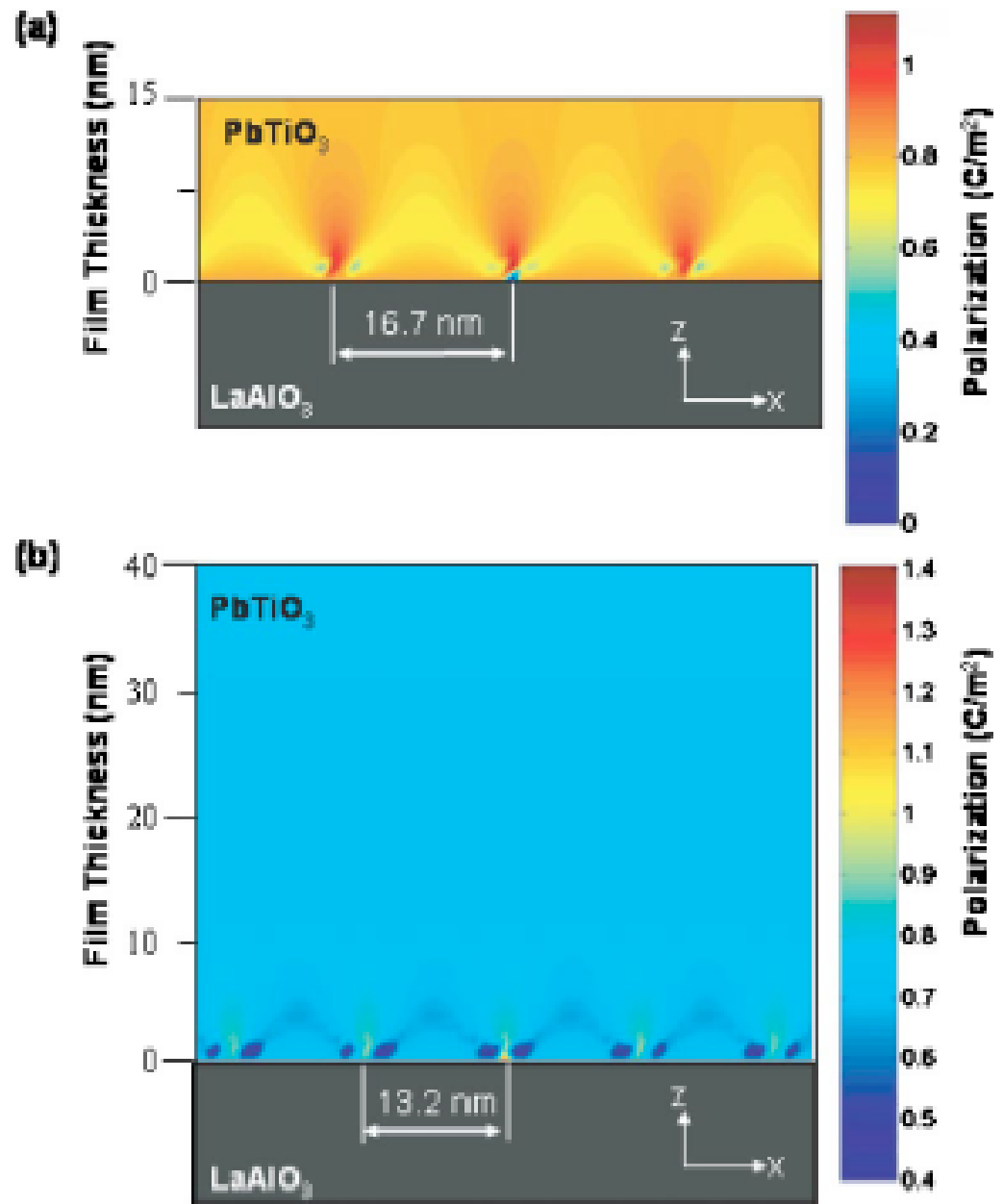


**vacuum annealed ( $10^{-6}$ ) Torr**

### 3) The polarization distribution around periodic misfit dislocations

(a) 15-nm-  
(b) 40-nm-thicks

(001) PbTiO<sub>3</sub> film  
on  
(001) LaAlO<sub>3</sub>  
substrate

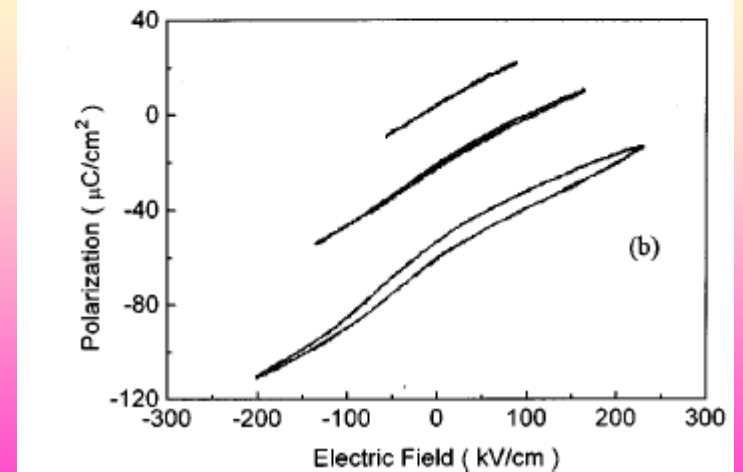
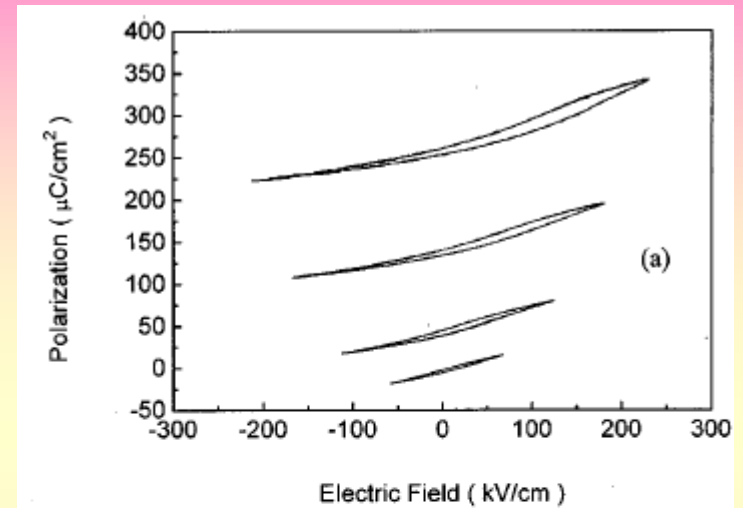
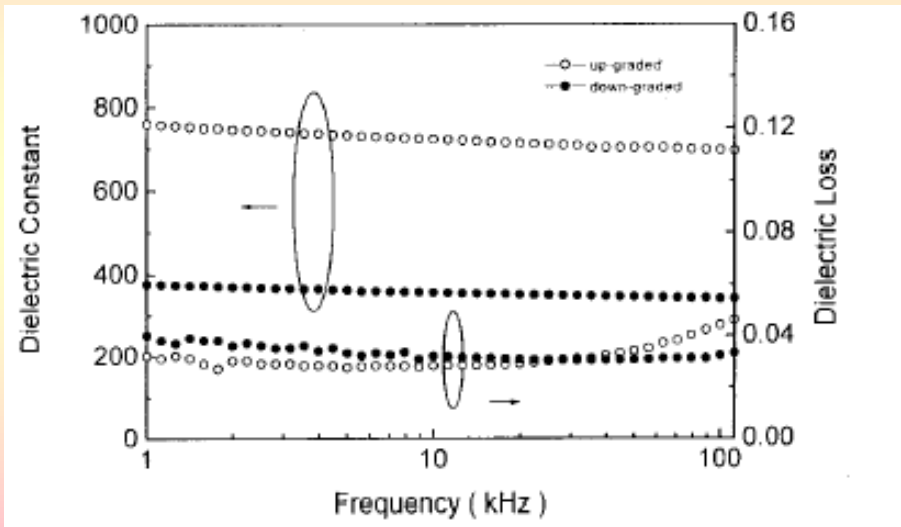


# Atomic-Scale Structure of Ferroelectric Thin Films

1. Materials:  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  (SBT) Thin Films with (001) orientation
2. Substrates: Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Si (100)
3. Growing Method : Pulsed Laser Deposition (PLD)

# 4) Compositionally Graded Ferroelectrics

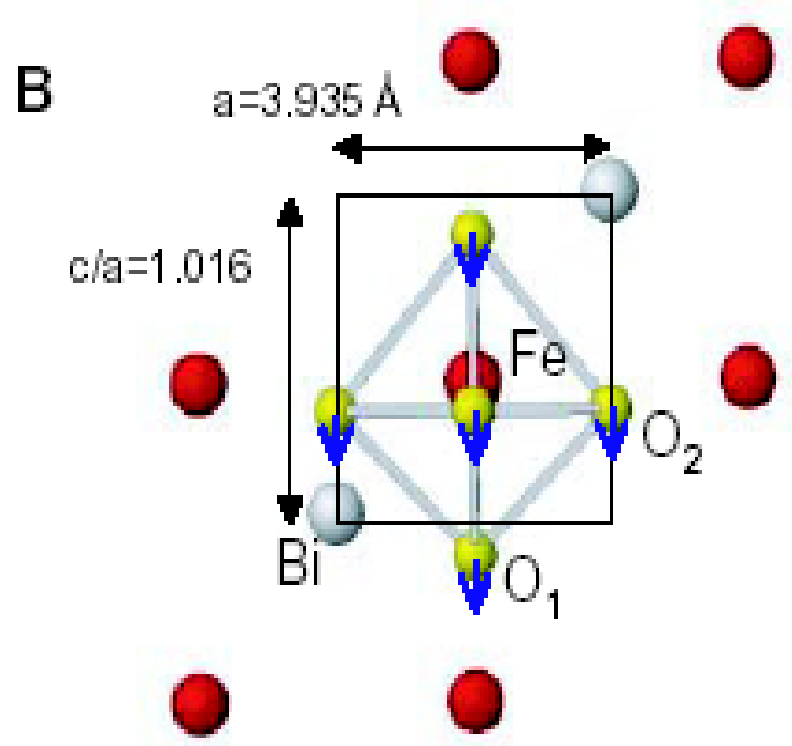
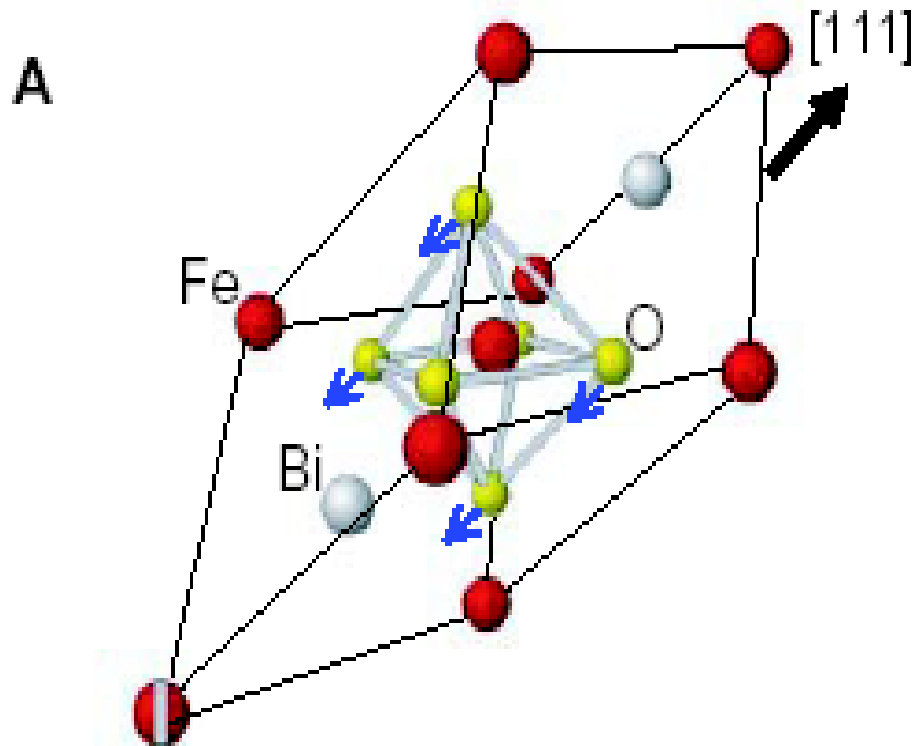
(Pb,La)TiO<sub>3</sub> thin films on Pt/Ti/SiO<sub>2</sub>/Si substrates

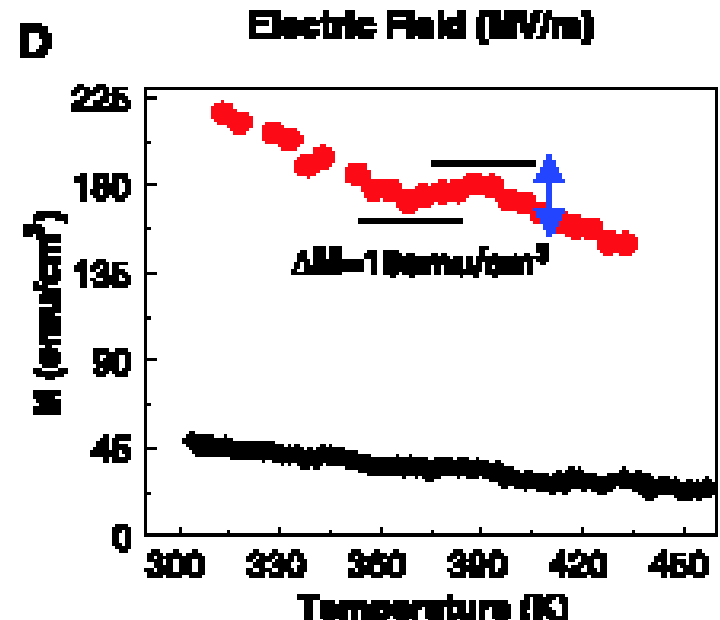
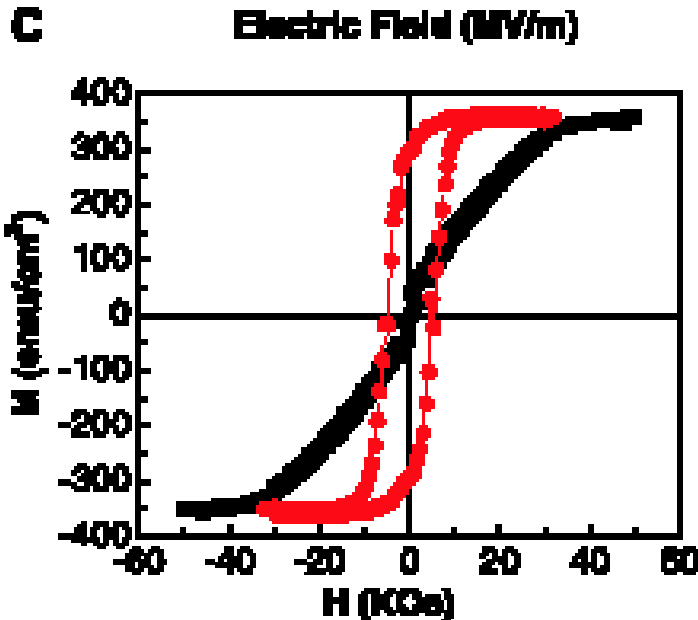
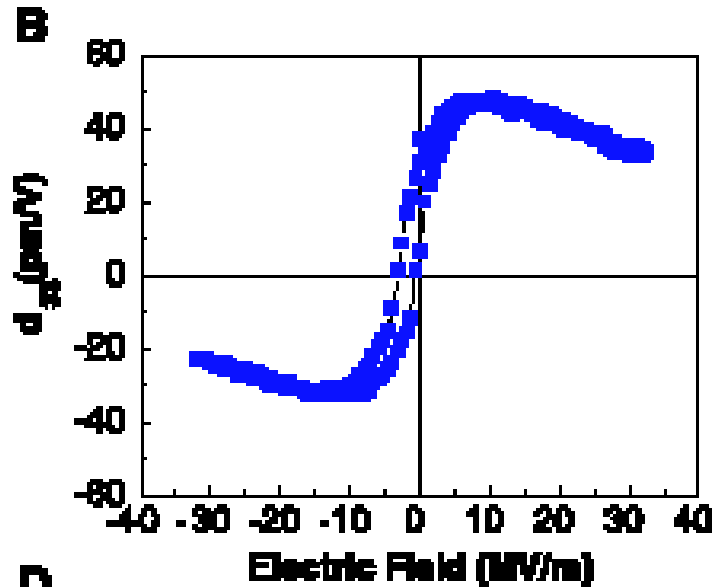
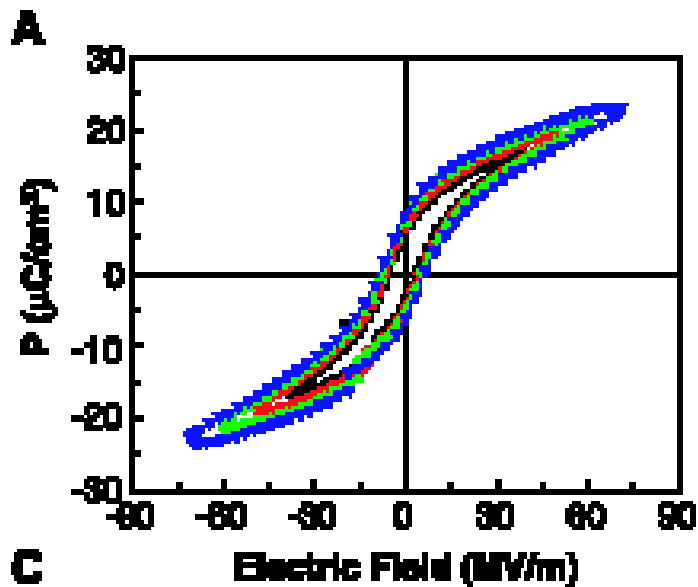


# 5. New material with new property

## --Ferroelectro-magnetic Materials

Simultaneous Ferroelectricity, Ferromagnetism





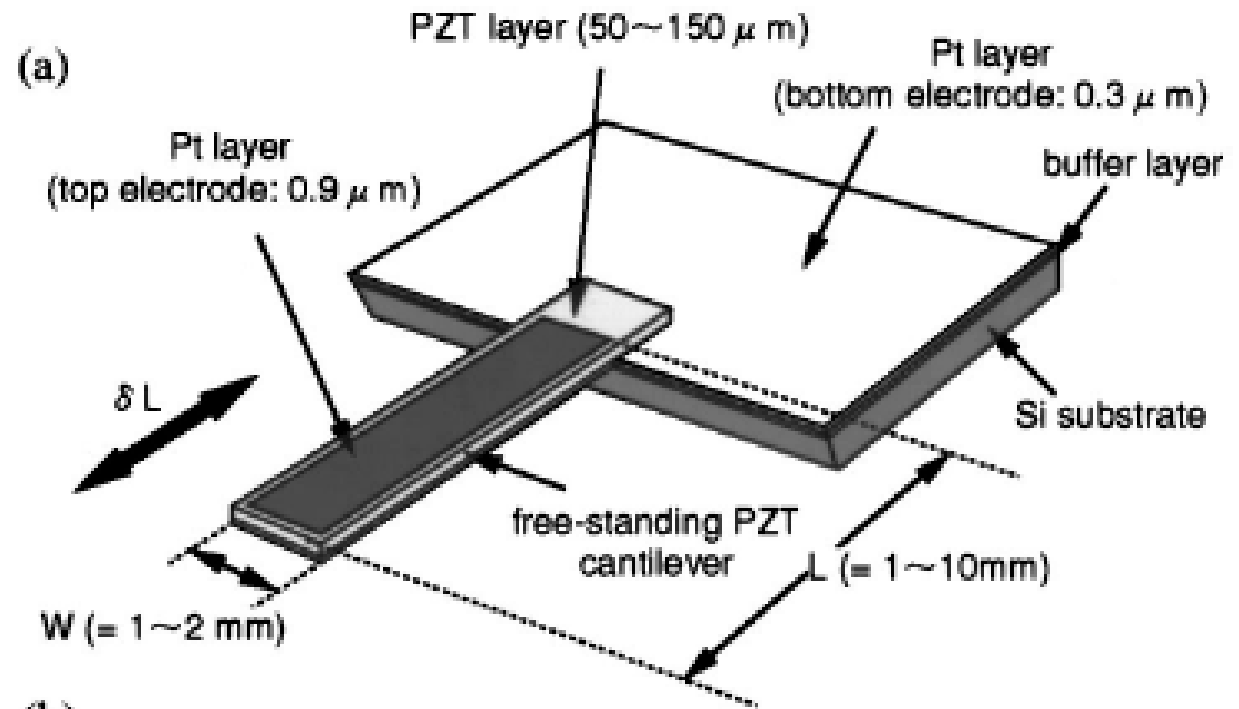


# Examining Devices

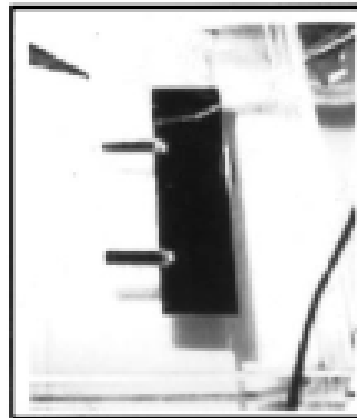
- 1. Transverse Electron Microscopy (TEM)
- 2. High-Resolution Transmission Electron Microscopy (HRTEM)
- 3. Dielectric Response (frequency, temperature)
- 4. Scanning Electron Microscopy (SEM)
- 5. Atomic Force Microscopy (AFM)
- 6. XRD (X-Ray Diffraction)



# Piezoelectric properties and poling effect of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ thick films

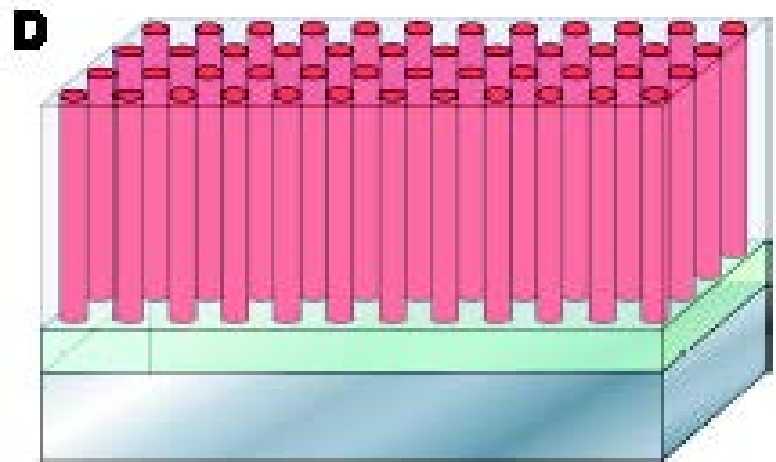
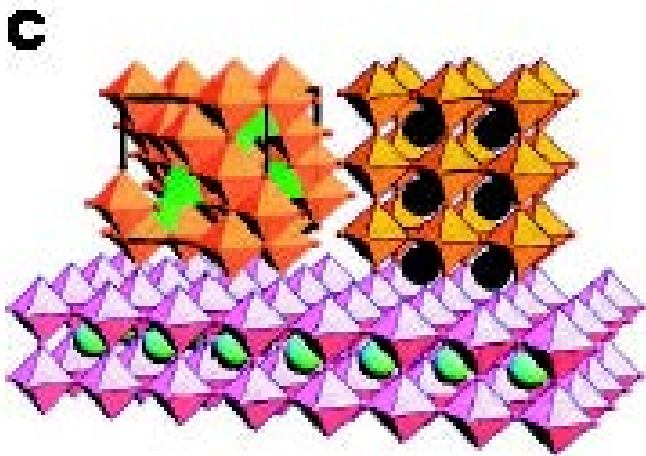
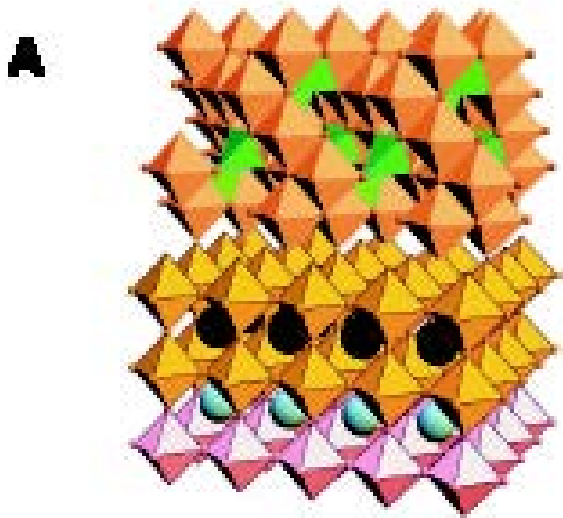


(b)



(c)





# 6. Possible Ferroelectric Chips

--a "disruptive" technology

- 1) Volatile memory chips: lose the data they store when the power is turned off. Most common types of volatile memory are DRAM and SRAM.**
- 2) Non-volatile memory chips: retain the data they store after the power is turned off. Most common types of volatile memory are flash and EEPROM.**

**3) DRAM (dynamic random access memory):**

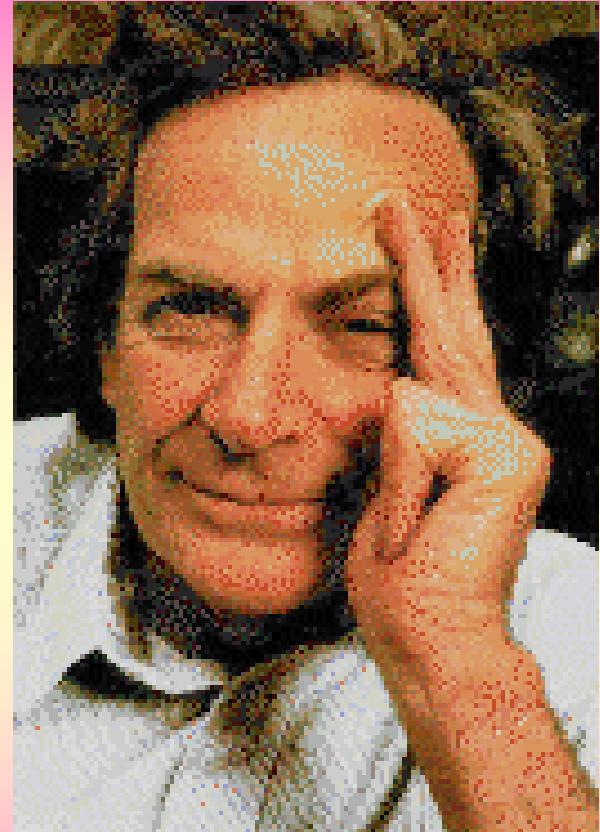
**high-density chips used in personal computers to store operating system and applications software. Store data in the form of electric charge on capacitors, which needs to be refreshed thousands of times a second (hence, "dynamic").**

**4) SRAM (static random access memory):**

**fast, relatively low-density memory used to store instructions for microprocessors or as a "scratchpad" in applications such as mobile phones. Needs battery back-up to retain contents.**

- 5).EEPROM (electrically erasable programmable read-only memory): type of chip used for example in conventional smartcards. Needs a high voltage to program and erase, hence not suitable for portable, battery powered applications.**
- 6).Flash: high-density memory used in particular to store bulk data such as digital photographs and mobile phone system software.**
- 7).System-on-chip: sliver of silicon on which are integrated microprocessor, memory and input-output circuits. Increasingly used in consumer electronics to lower cost, reduce power consumption and increase flexibility.**

# Thanks for your attention!



## Nothing is Impossible!!!