清华大学 Tsinghua University
新型陶瓷与精细工艺国家重点实验室
STATE KEY LABORATORY OF NEW CERAMICS & FINE PROCESSING

高介电温度超稳定型$BaTiO_3$基细晶陶瓷多维设计策略：利用核壳结构调控和多离子掺杂

Temperature ultra-stable $BaTiO_3$-based ceramics with near-nano grains via the core-shell structure design and controlled grain growth

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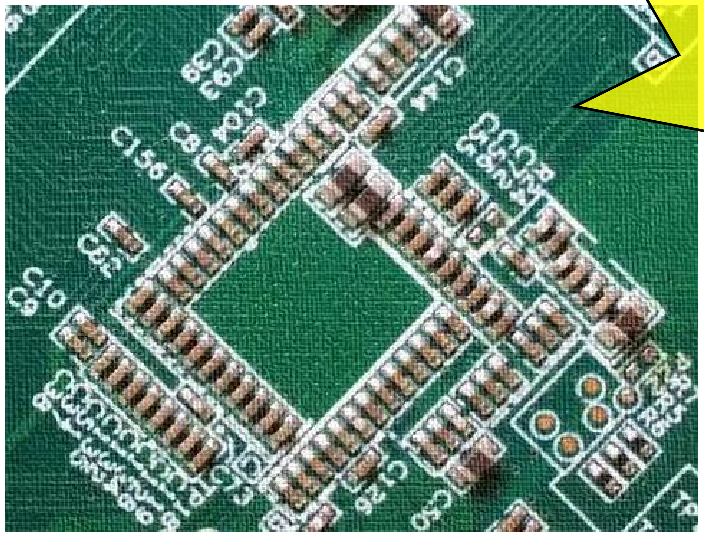
CONTENTS

1. 研究背景

Research background

作为现代电子工业的"细胞级"元件，MLCCs
占据全球陶瓷电容器市场93%的份额

多层陶瓷电容器
Multilayer ceramic capacitors：MLCCs



在电路板上的MLCCs

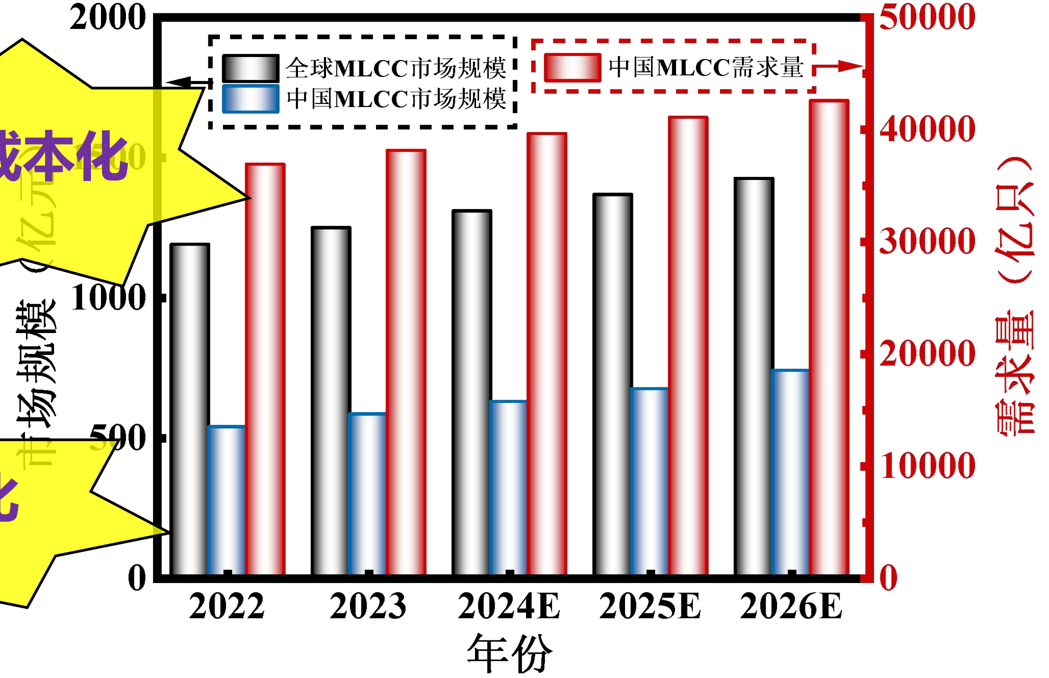
温度稳定性

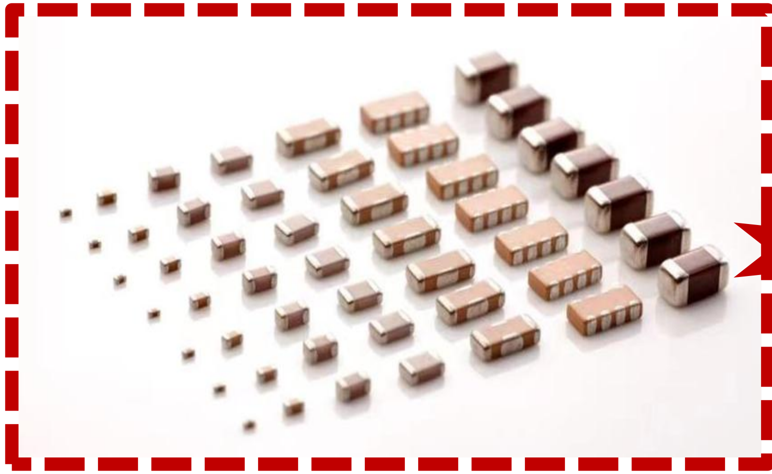
低成本化

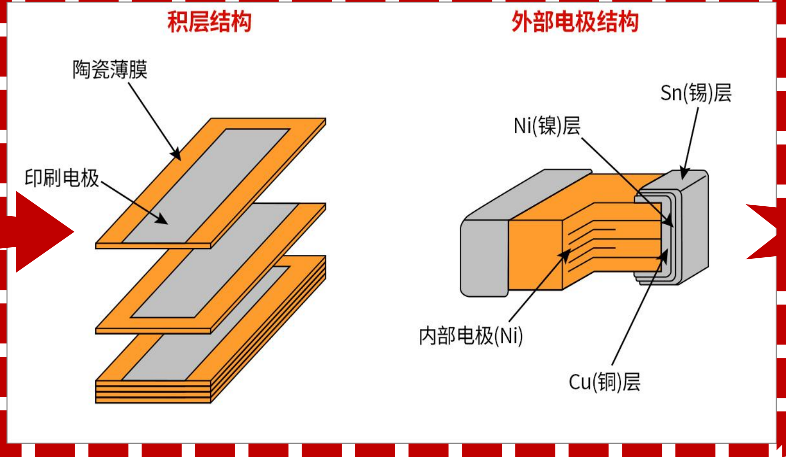
在新能源汽车电力系统（单车用量超10,000颗）、5G基站（单站用量达15,000颗）、AI服务器等等需求驱动下

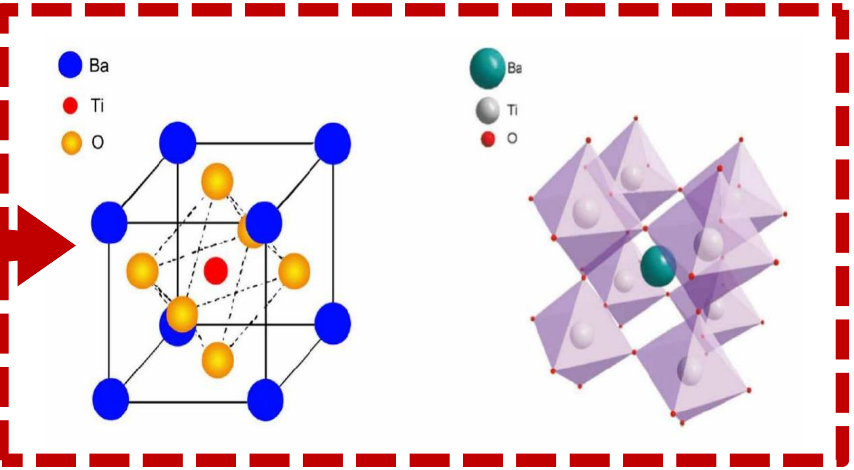
小型化

高电容化

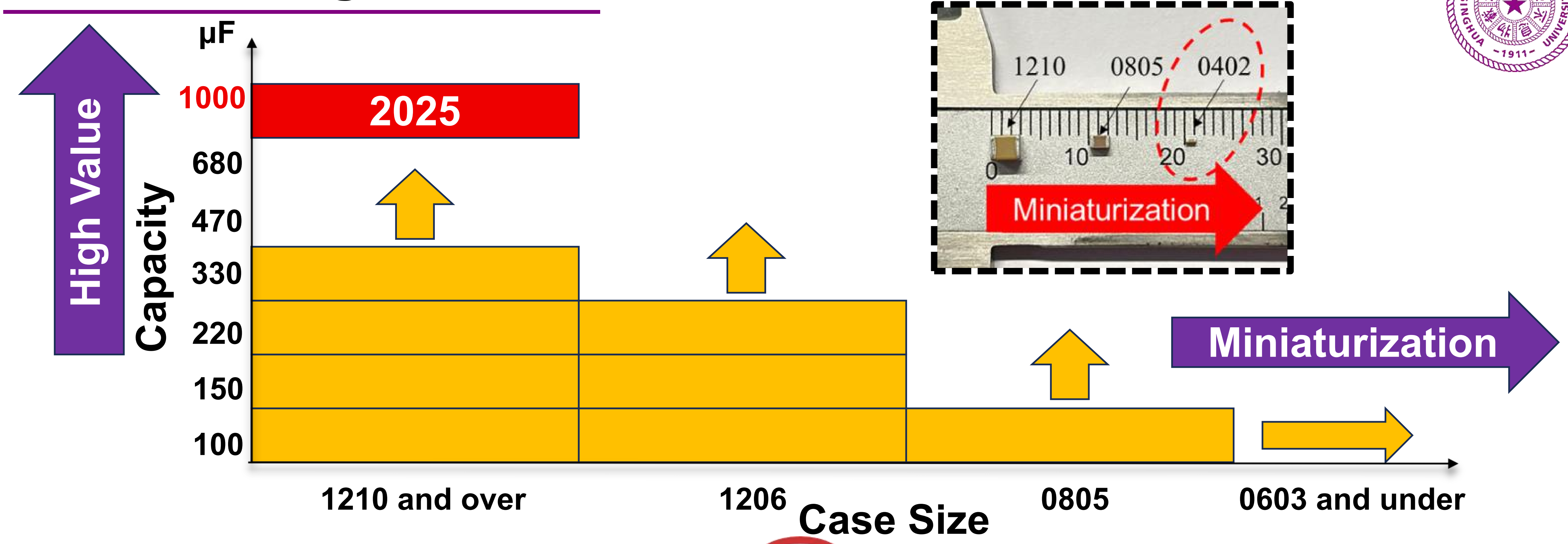


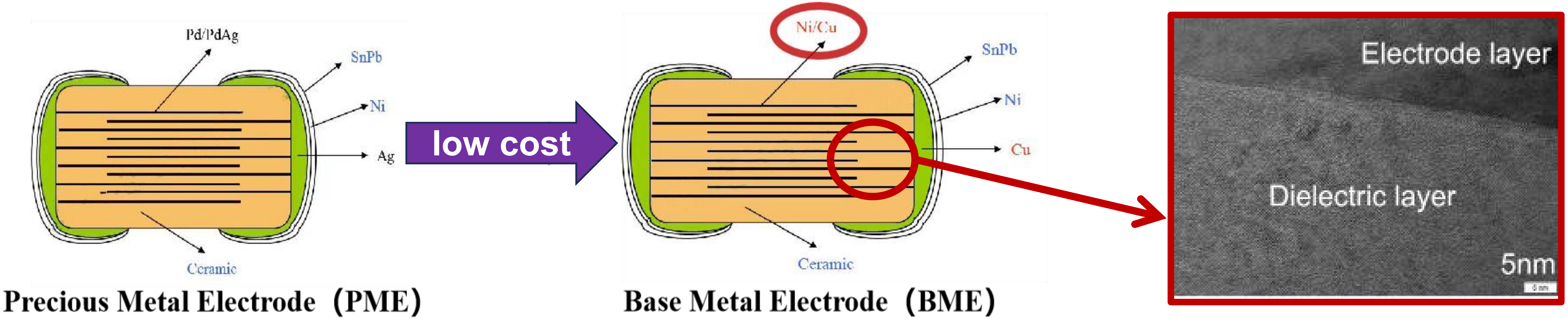






Research background





Research background

一类陶瓷电介质

成本高、介电常数小，但稳定度极其高

用三位大写字母表示

第一位字母		第二位字母		第三位字母	
代码	有效数字（ppm/℃）	代码	乘数	代码	误差范围（ppm/℃）
C	0.0	0	-1.0	G	30
M	1.0	1	-10	H	60
P	1.5	2	-100	J	120
R	2.2	3	-1000	K	250
S	3.3	4	-10000	L	500
T	4.7	5	+1	M	1000
U	7.5	6	+10	N	2500
		7	+100		
		8	+1000		
		9	+10000		

二类陶瓷电介质

相对来说具有成本优势、高介电常数，但稳定性差

用三位大写字母表示

第一位字母 表示最低工作温度		第二位字母 表示最高工作温度		第三位字母 表示容量变化范围	
代码	下限温度	代码	上限温度	代码	最大变化率 ΔC/C
X	-55℃	2	+45℃	A	±1.0%
Y	-30℃	4	+65℃	B	±1.5%
Z	+10℃	5	+85℃	C	±2.2%
		6	+105℃	D	±3.3%
		7	+125℃	E	±4.7%
				F	±7.5%
				P	±10.0%
				R	±15.0%
				S	±20.0%
				T	+22~-33%
				U	+22~-56%
				V	+22~-62%

Electronic Industries Association (EIA)

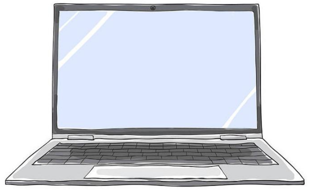
电子工业协会规定标准

例：C0G表示温度系数为(0±30)ppm/°C（即-55°C~125°C：$\Delta C/C_{25°C} \le 0.54\%$）。C0G与NP0是不同标准体系的表示方式，实质上是等同的

例：X7R表示-55°C ~ 125°C温度区间内，以25°C室温为基准,容量$\Delta C/C_{25°C}$允许变化范围±15%

Research background

研究现状



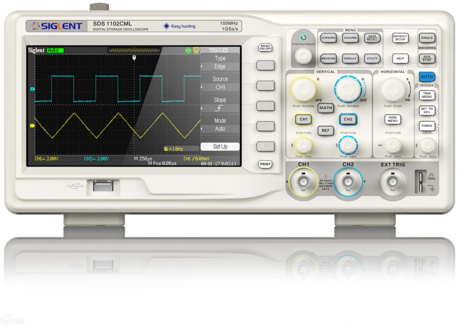
各类电子设备都开始考虑到在极端温度的工作环境下运转，随之对电介质宽温稳定性也提出了要出。

X7R → X8R → X9R

在拓宽工作温度范围的路上颇有成效

研究缺口

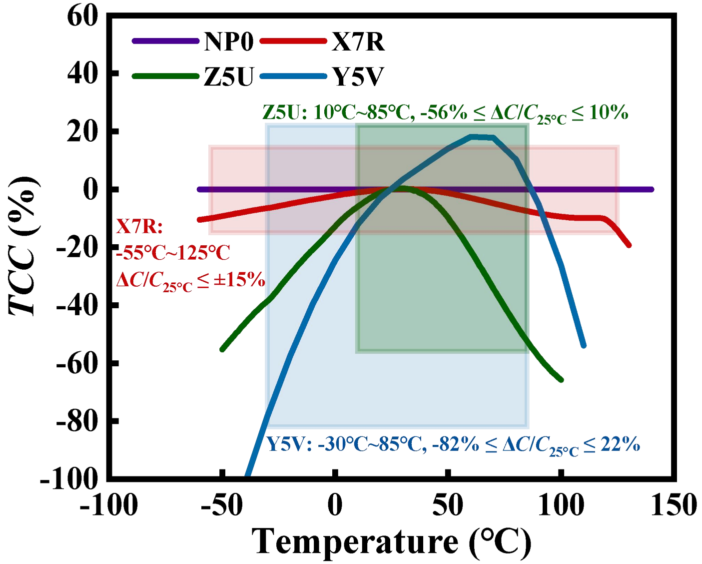
可±15%的容温变化率并不足够



要寻求在同样工作温度范围内，可以在更高精密电子设备中使用的电容器介质材料

然而这些设备的MLCC介质层却被高成本、低电容量的一类陶瓷电介质（NP0等）所垄断

满足±2%甚至更低容温变化率的温度超稳定型介电陶瓷



J. M. Whiteley, et al. Journal of the Electrochemical Society, 2014, 161(12): A1812-A1817.

GAO L, et al. Science China Technological Sciences, 2023, 66(7): 2059-2068.

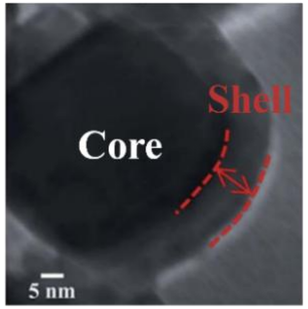
2. 设计策略

Strategy

提高介电温度稳定性的重要手段：

(a)

(b)



“壳”选用介电常数与“核（$BaTiO_3$）”相差较大的材料 → 在具有核壳结构的陶瓷材料中，介电常数是核部与壳部的介电特性相叠加 → 表现为**居里峰的展宽**

“壳”选用与“核（$BaTiO_3$）”具有不同相结构的材料 → 构筑“异相共存”的复合界面 → 包覆后造成的核壳各微区分布不均匀，引起在相变区的扩散，相变温度点呈空间分布（**弥散相变**）

采用固相烧结法，在成瓷前通过高温将预包覆好的“壳”离子更易扩散进“核” → 壳到核具有连续的浓度梯度和化学均匀性 → 完成在钙钛矿晶格中的离子置换占位，产生**纳米微区**，破坏长程有序

K. J. Kim, Advanced Energy Materials, 2020, 11(1): 2002689

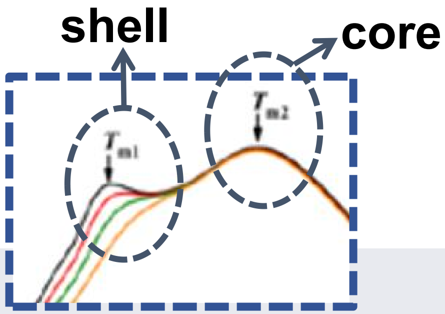
Strategy

其中对“核”中多离子B位掺杂设计

$$CaSiO_3 + Ti_{Ti} + O_o \rightarrow Ca''_{Ti} + V\ddot{O} + TiO_2 + SiO_2$$

$$Y_2O_3 + 2Ti_{Ti} + O_o \rightarrow 2Y'_{Ti} + V\ddot{O} + 2TiO_2$$

$$MgO + Ti_{Ti} + O_o \rightarrow Mg''_{Ti} + V\ddot{O} + TiO_2$$



将Ca离子引入至B位 → **降低陶瓷的第二相变点(~ -90℃)**

具有不同价态和半径的B位离子掺杂会产生纳米极性微区（PNRs） → **破坏长程有序并引发弛豫态**

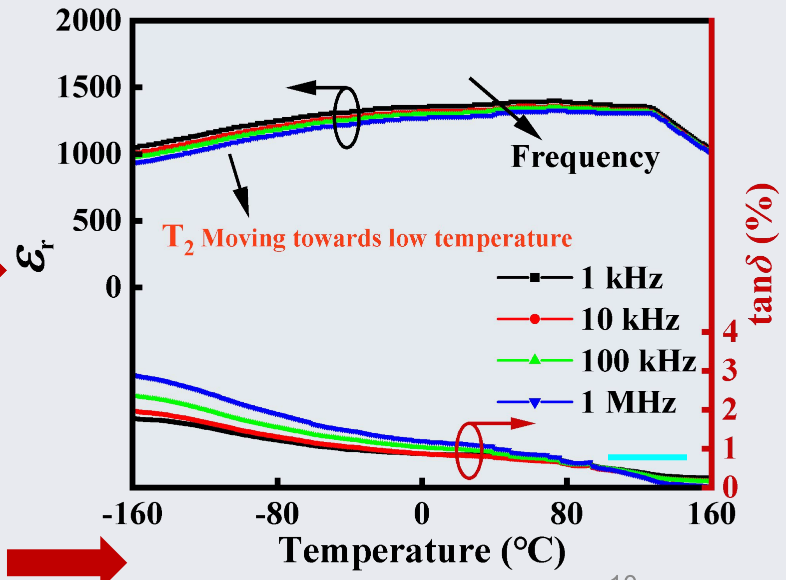
使得体系得以在相对较低的温度进入到对称平衡结构 → **导致陶瓷的四方相性和Tc降低**

核壳双峰高度往往不一致，并达不代表真正平坦的介温曲线

外来低介物质会压低改性陶瓷的介电常数

→ **调控好双峰的高度，找出最适合掺杂比例。**

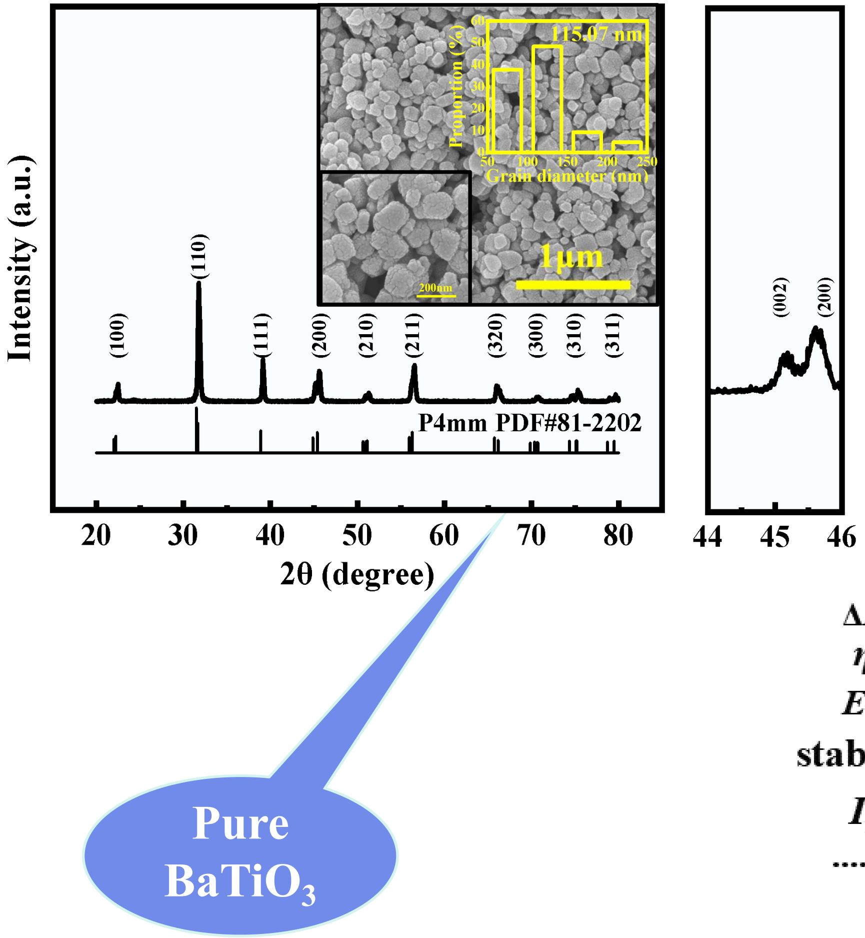
固相法所形成的包覆效果往往不如液相法 → **在烧结前通过预烧的方式预包覆一层壳。**

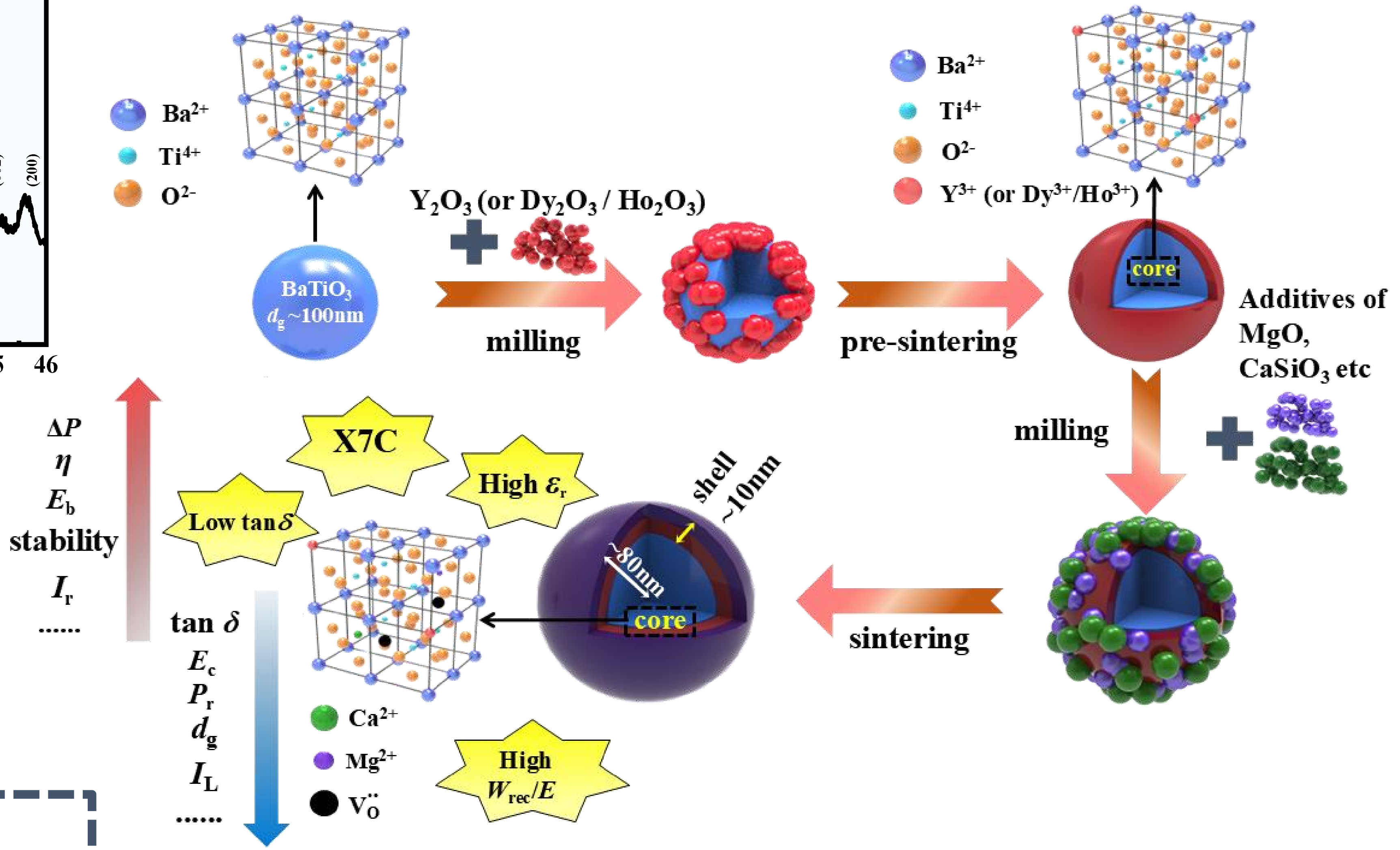


获得足够宽且平坦的介电温谱曲线

Deiseroth, et. al. Allg. Chem, 2011, 637, 1287-1294.

Strategy



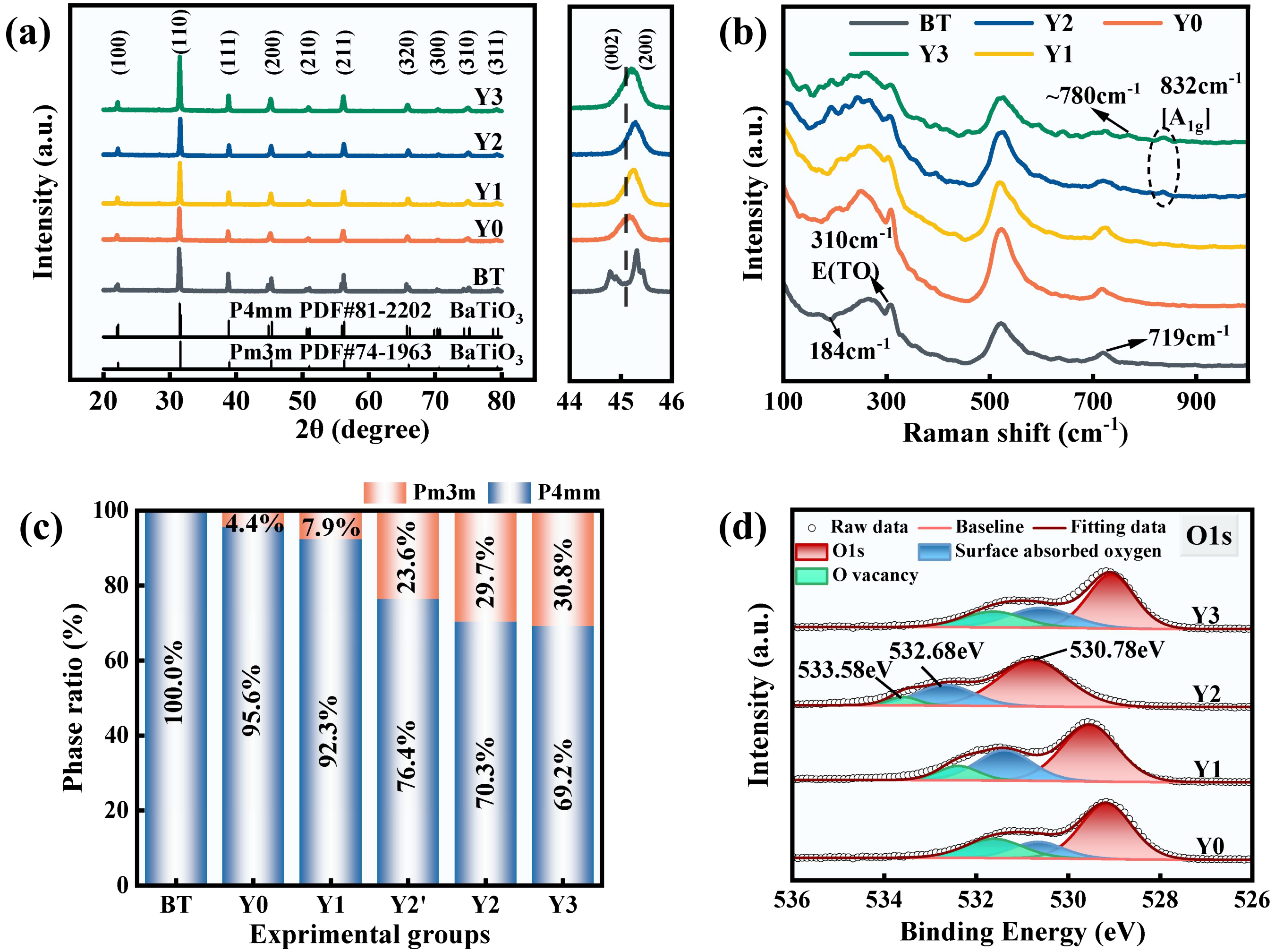


设置对照组与实验组：

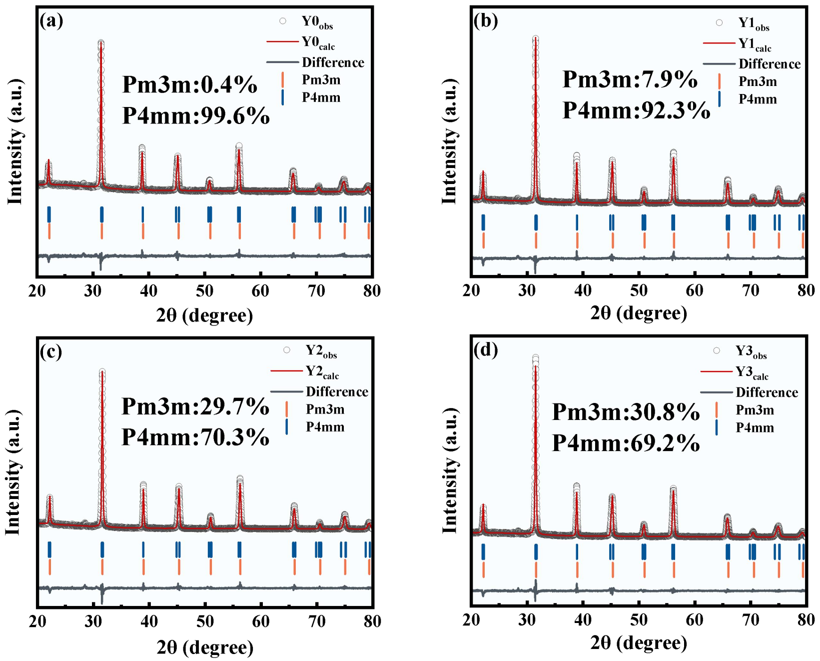
BT ；Y0 ；Y1 ；Y2 ；Y3 。

3. 研究结果

Results



Y2有着最低的氧空位浓度

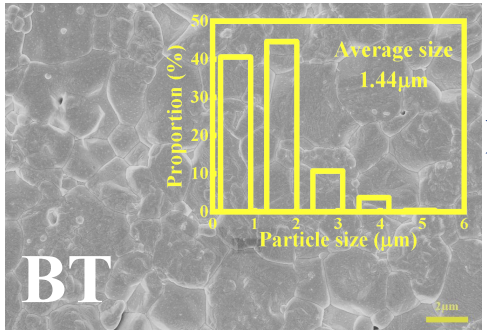


- 通过掺杂，陶瓷在室温下展现**明显的立方相性**，为**赝立方相——弛豫态的象征**。
- 出于电中性和维持晶胞体积的目的，**Y^{3+}在A位上的富集**会导致**Ca^{2+}更倾向占据B位**，且当Y^{3+}在A位上达到固溶极限时，会**使得部分Y^{3+}开始置换Ti^{4+}**，即发生自补偿机制：

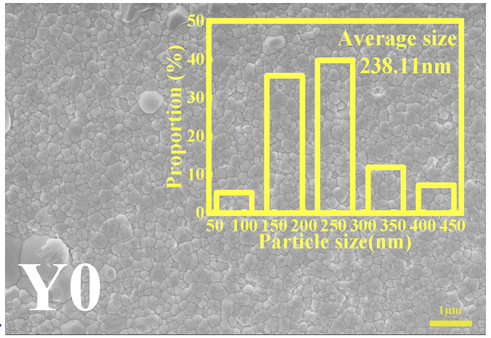
$$Y_2O_3 + Ba_{Ba} + Ti_{Ti} \rightarrow Y_{Ba}^{\cdot} + Y_{Ti}^{'} + BaTiO_3$$

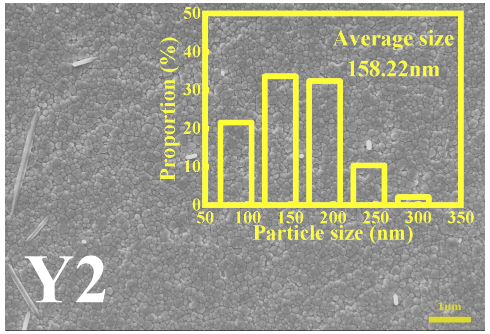
而这个过程会**消耗氧空位浓度**以**提升其电学性能**

Results

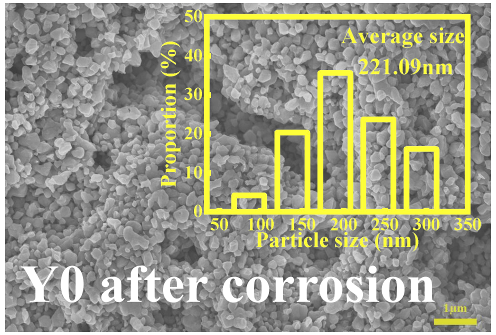


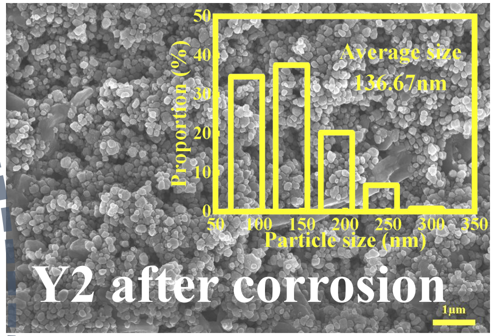
细晶效果明显

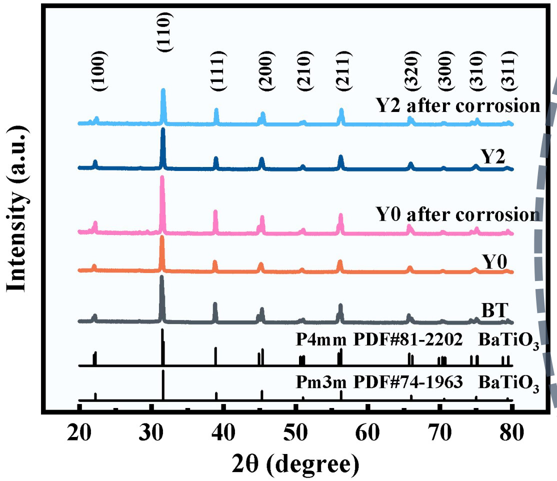


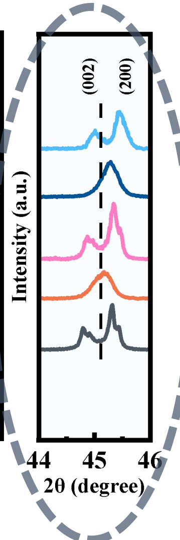


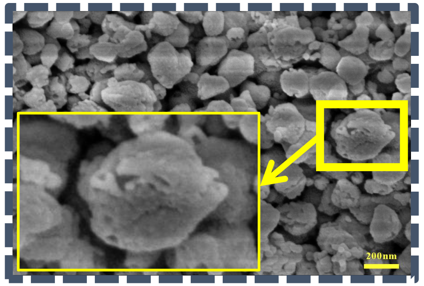
使用浓度为5%的HCl和HF混合溶液对陶瓷块体进行腐蚀









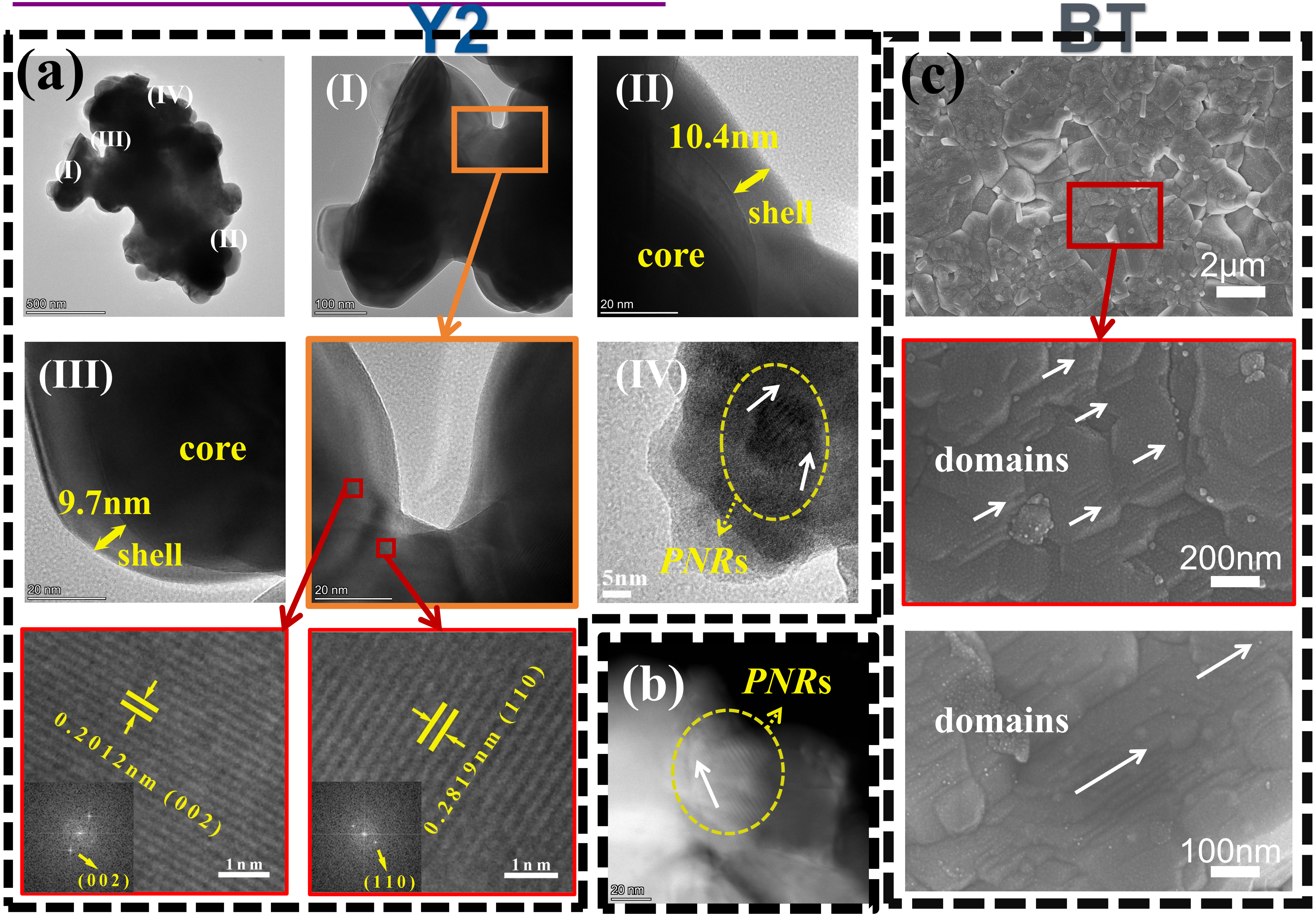


通过酸溶液腐蚀掉壳层前后的粒径尺寸(如对Y2（158.22nm-136.67nm）/2 = 10.775nm算出壳层的厚度），通过**体积公式**计算结果符合**精修所得Pm3m相所占比例29.7%**。

揭示着**立方相含量**大多是由核壳结构的**壳层**所提供

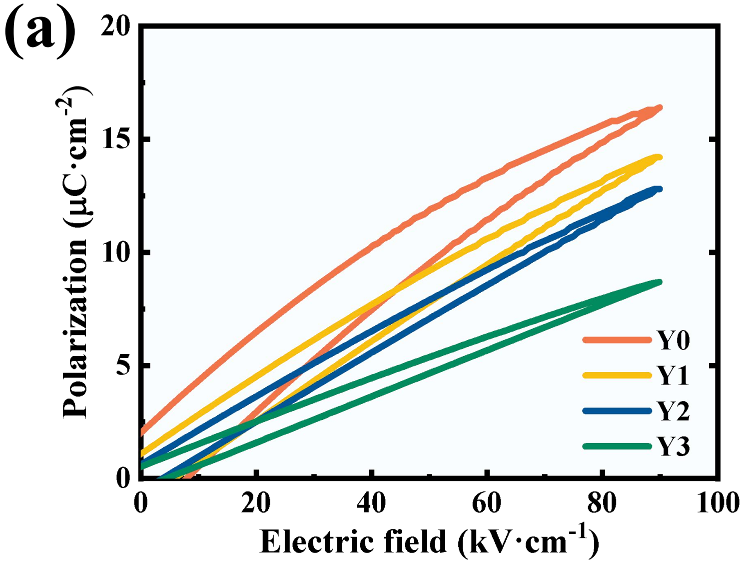
30s的酸腐蚀后

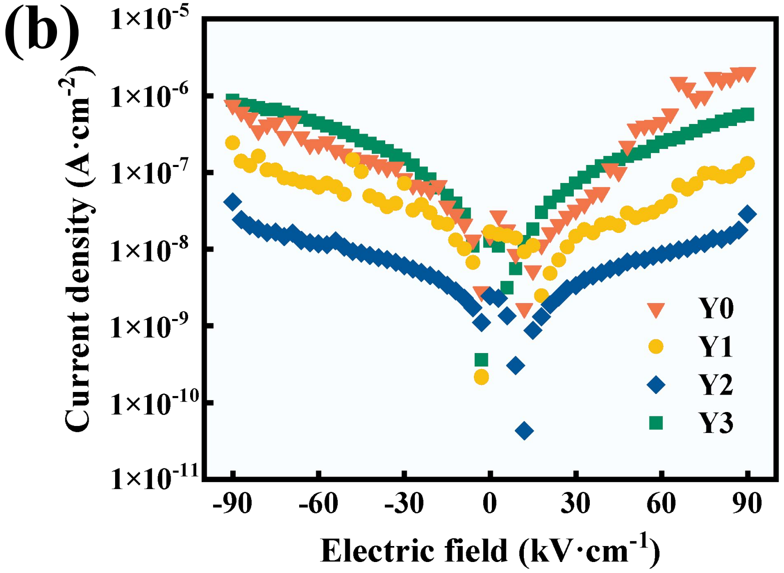
Results



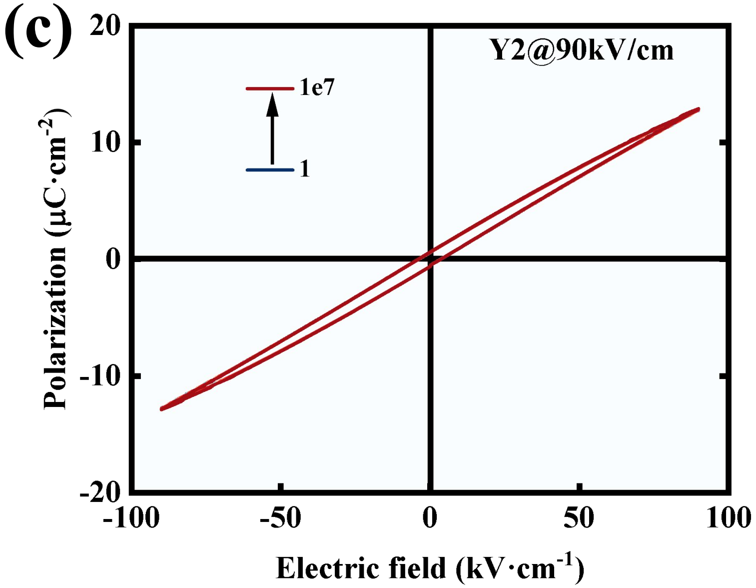
铁电畴从**长程有序**转变为**长程无序且短程有序的纳米畴**代表着**铁电态**到**弛豫态**的过渡，从而获得优异**介电温度稳定性**以及**良好的储能性能**。

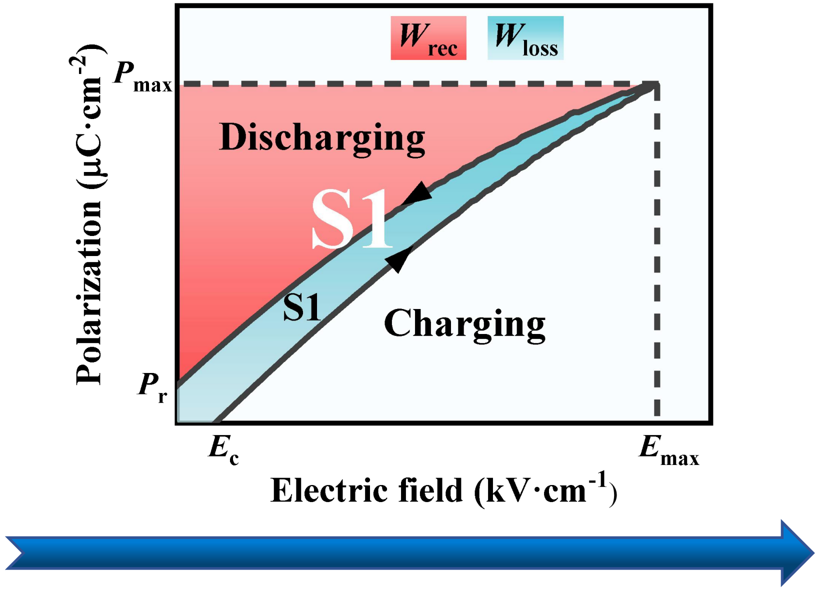
Results



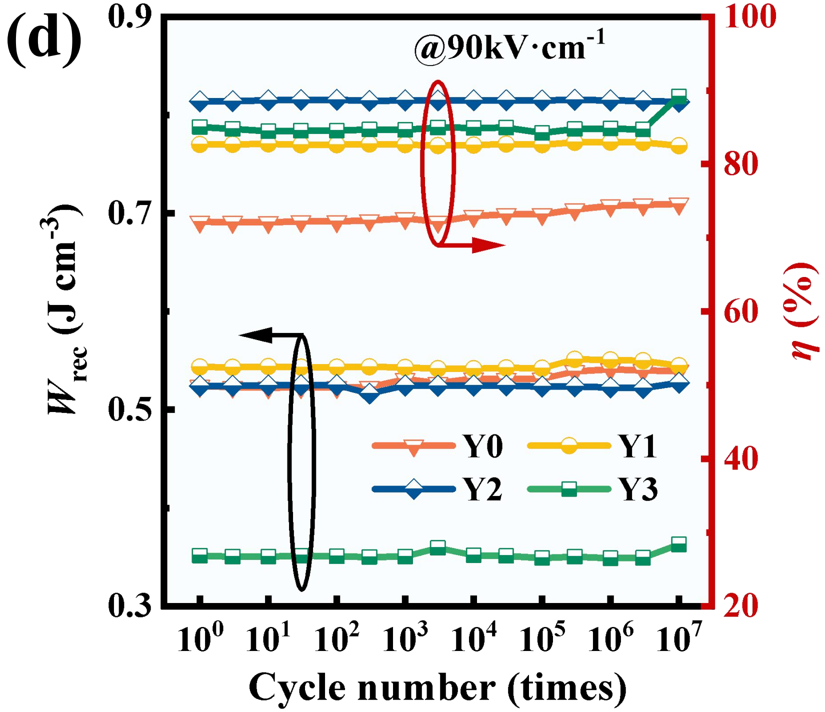


最优例Y2：在E_{max}=240kV/cm下，W_{total}=3.79J/cm^3，W_{rec}=3.15J/cm^3，η=83.19%。**耐疲劳性能极好：在循环10^7次后，W_{rec}和η都能维持在99%以上**，同时还具有出色的温度和频率稳定性以及最低的漏电流密度。

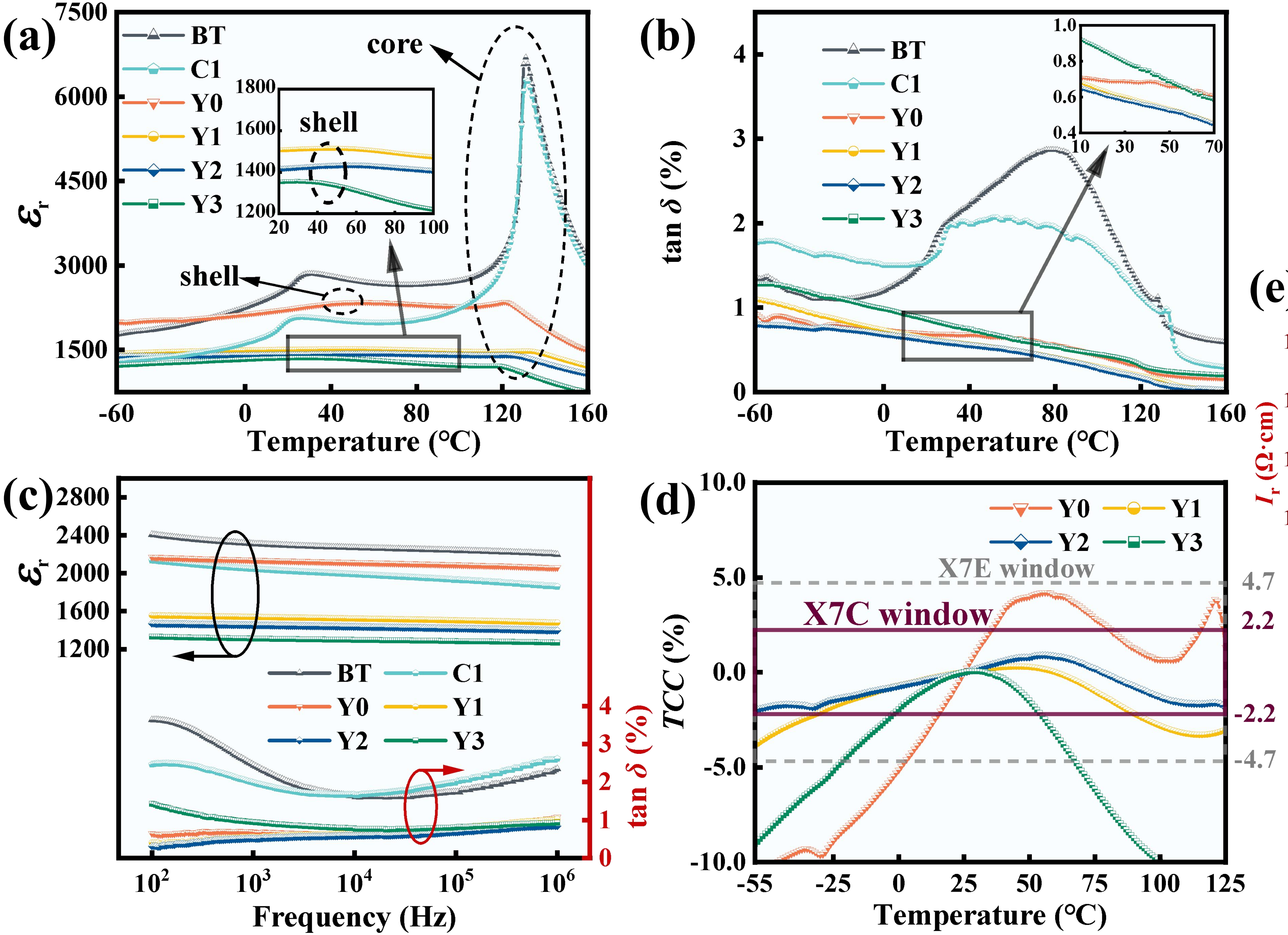




利用积分面积计算

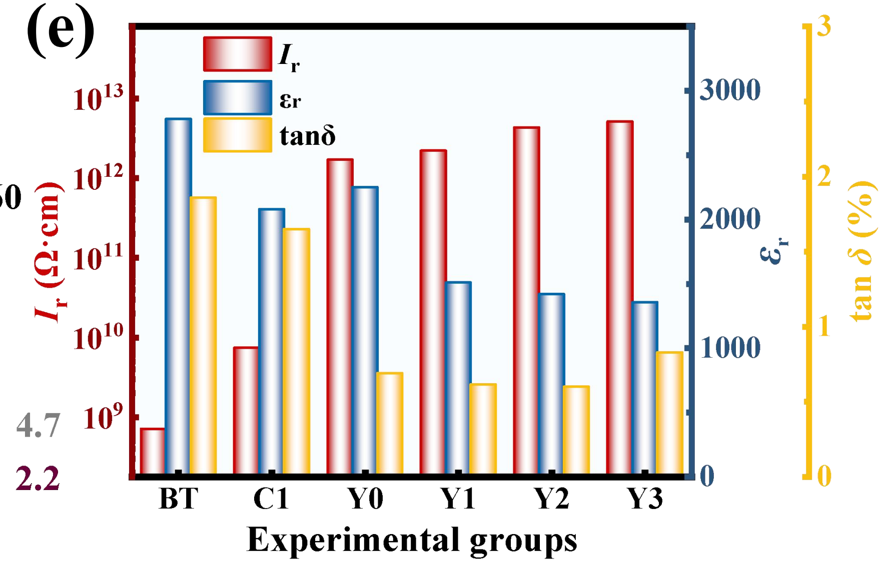


Finished works



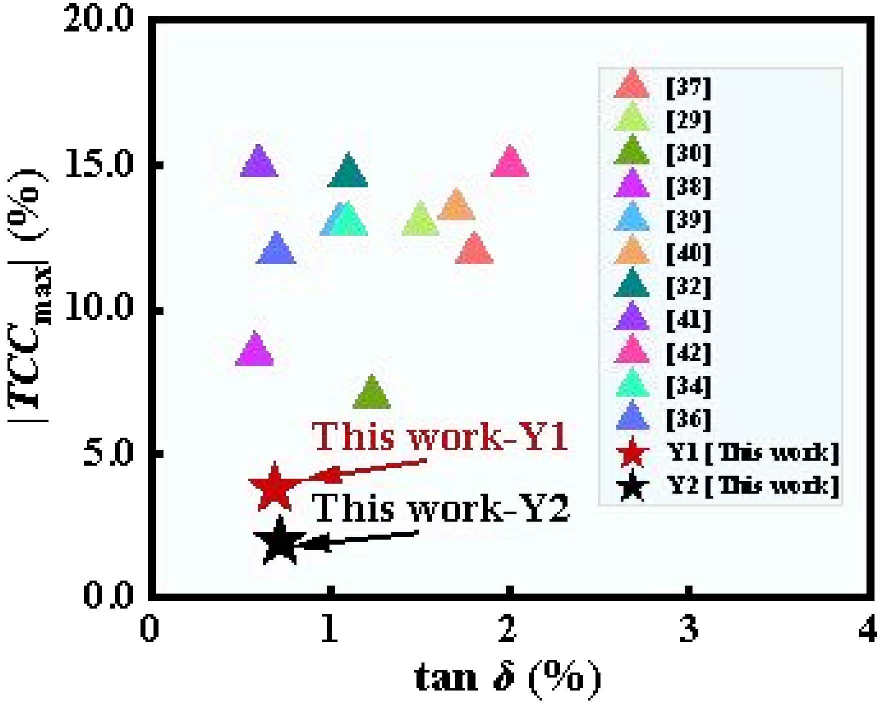
最优例Y2：

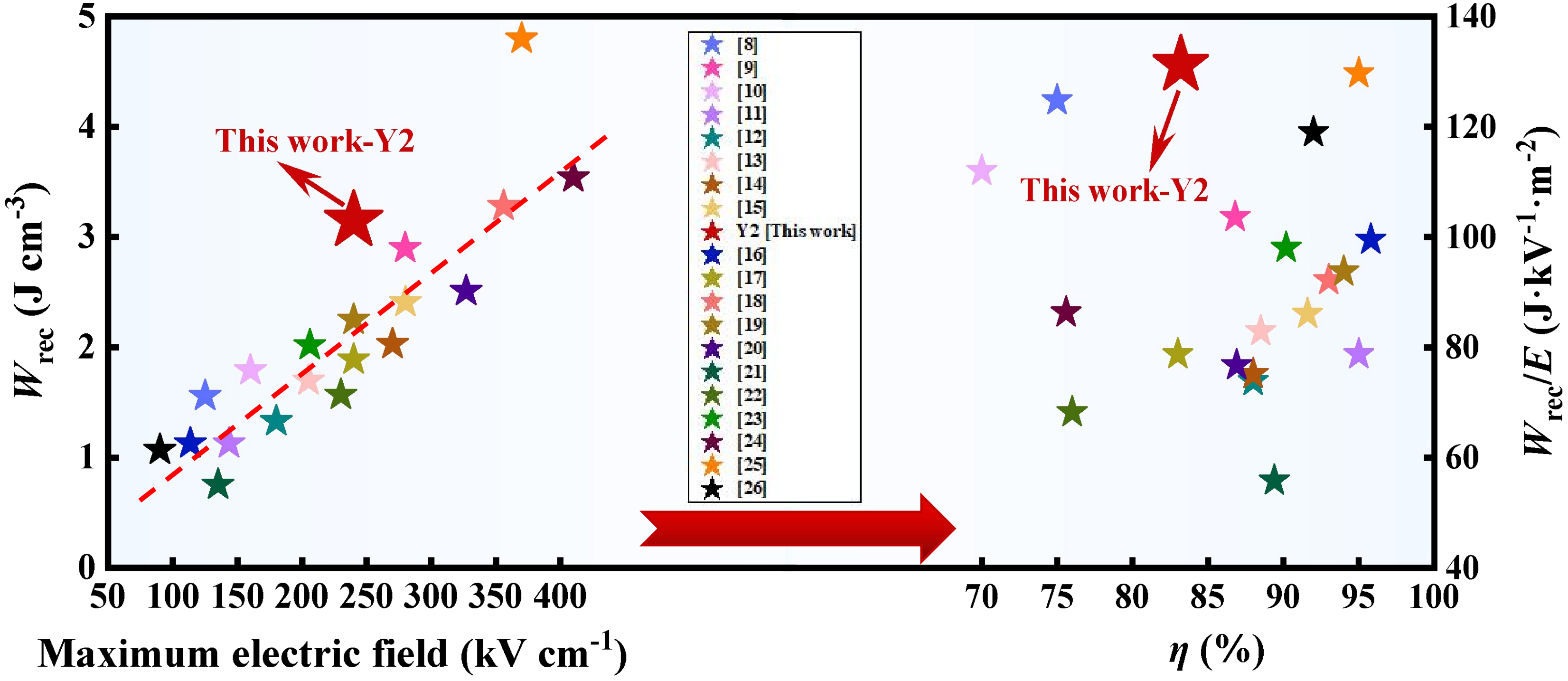
$\varepsilon_r = 1418$；
$tan\delta = 0.71\%$；
-55°C~125°C：
TCC: $\Delta C/C_{25°C} \leq 1.97\%$



此外还有着优异的介电频率稳定性以及高绝缘电阻率(4.3×10^{12}Ω·cm)

Results





相比其它所报道的温度稳定型
$BaTiO_3$陶瓷，Y2有着显著的优势。

$\xi = W_{rec}/E$ =131.25（J/kV·m²）
揭示着每单位电场强度下的放电能量密度

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Results

- 准纳米细晶：平均晶粒尺寸为158.2nm，符合当今最小MLCCs对介质层陶瓷晶粒尺寸小于200nm的要求。
- 优异的储能性能：在240kV/cm的中低电场下有着高的放电能量密度$W_{rec}=3.15 J/cm^3$，即高的比电场能量密度ξ（$W_{rec}/E=131.25$ J/kV·m²），同时还维持着$\eta=83.19\%$较高效率，此外，在循环10^7次后，W_{rec}和η都能维持在99%以上，有着出色的耐疲劳性。
- 出色的介电性能：-55℃~125℃，$\Delta C/C_{25°C} \leq \pm 1.97\%$，满足X7C标准，高介电常数（~1418），低介电损耗（0.007）以及高的电阻率（$4.3\times10^{12}\Omega\cdot cm$）。

已授权发明型专利

【1】一种低成本、低损耗和温度超稳定型介质材料及制备方法

授权公告号CN 116239378 B

已实审发明型专利

【1】一种高储能密度、高介宽温稳定型$BaTiO_3$基电介质材料及制备方法

专利号：2024103553077

【2】一种钛酸钡基多层复合吸波材料及其制备方法

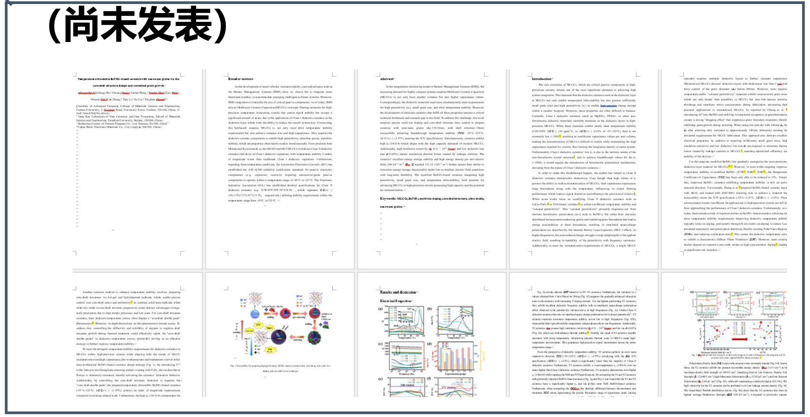
专利号：202410091713.7

相关工作已发表论文：

【1】 Colossal permittivity and excellent temperature stability of $BaTiO_3$ based fine ceramics with controlled grain growth. Ceramics International, 2024, 50(7, Part B): 11980-11988.

【2】Temperature-stable dielectric properties of Nb_2O_5-doped $BaTiO_3$ based ceramics with fine grain via controlling grain growth. Ceramics International, 2025, Available online 26 March 2025: 0272-8842.

已完成手稿（尚未发表）



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