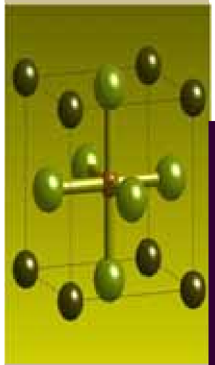
2012年9月11日（水）
14:50 – 15:20

SPring-8粉末材料構造解析研究会（第4回）
～ 材料構造解析のための最新手法情報 ～
（社）日本化学会　化学会館7Fホール

セラミックス材料における優れた誘電特性創出のための構造物性研究

黒岩　芳弘
広島大学 大学院理学研究科 物理科学専攻
kuroiwa@sci.hiroshima-u.ac.jp



Structural Study of Ferroelectrics at BL02B2 in SPring-8

イントロダクション

－強誘電体と反強誘電体－

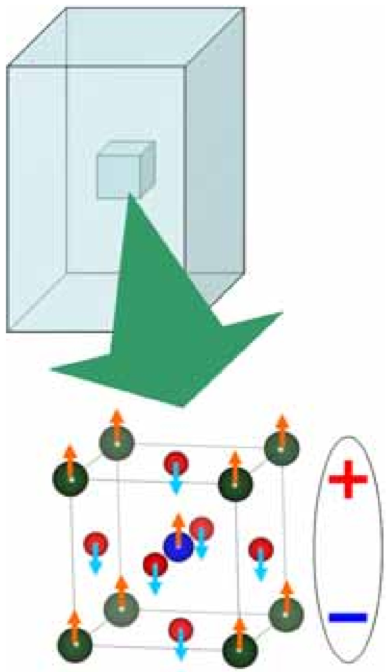
強誘電体

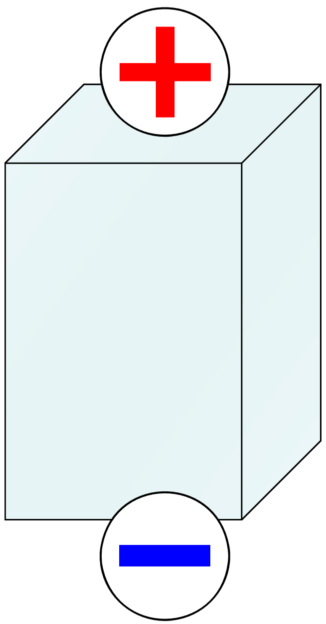
強誘電性

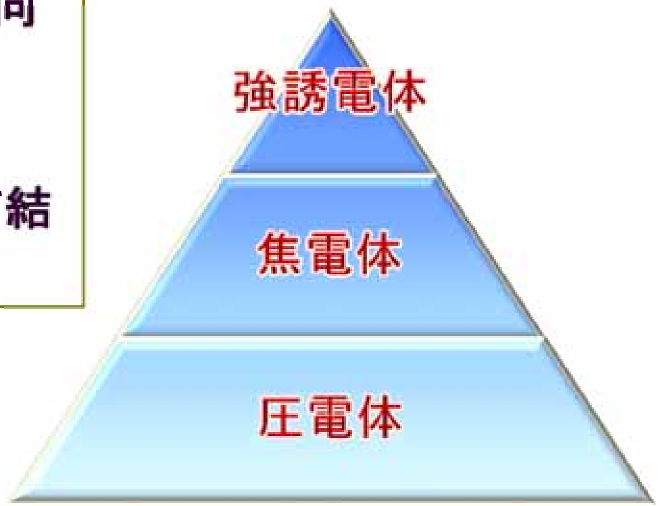
- 電圧ゼロでも電荷を蓄える機能をもっている.
- 電圧を印加する方向を逆転することにより，分極方向を変化させることができる.

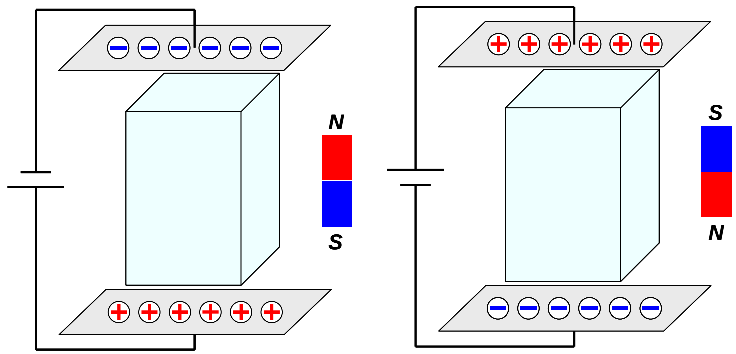
圧電性

- 電圧を印加すると結晶が歪む．一方，外力を加えて結晶歪ませようとすると分極する.





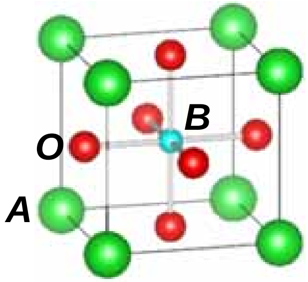




Perovskite-type Oxide

- antiferrodistortive and ferrodistortive instabilities inherent in prototype structure

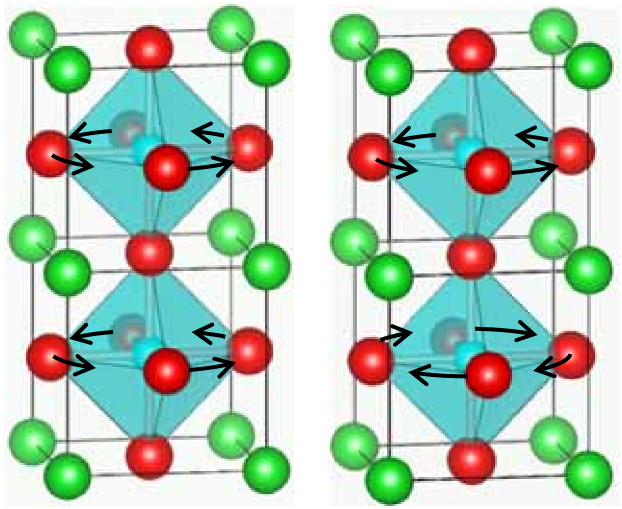
***Prototype structure of ABO_3 perovskite-type oxide*: Cubic**



A: (0, 0, 0)
B: (0.5, 0.5, 0.5)
O: (0.5, 0.5, 0), (0.5, 0, 0.5), (0, 0.5, 0.5)

Antiferrodistortive instability

***B*O_6 tilt driven perovskite**

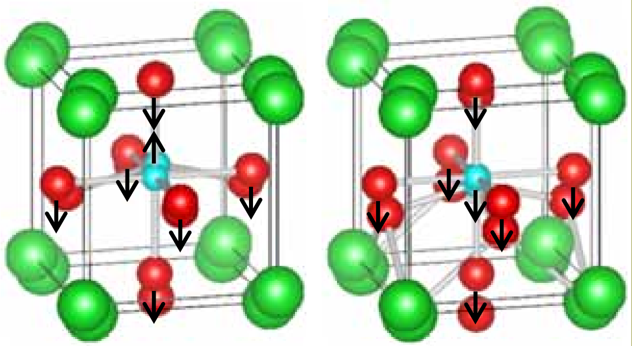


M_3 mode **R_{25} mode**

If *A* is Pb or Bi, *A*-site off-centers

Ferrodistortive instability

***B*-site off-centering driven perovskite**



Slater mode **Last mode**

ペロブスカイト型誘電体の
プロトタイプ構造の特徴と相転移

―トレランスファクターと相転移―

― PZTのMPB形成とプロトタイプ構造の特徴―

Mode Classification by Tolerance Factor

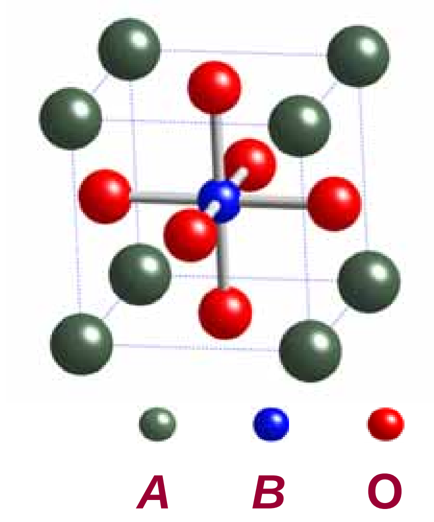
- relationship between crystal structure and phase transition –

simple classification to predict phase transitions

Tolerance factor *t* :

$$0.8 \le t = \frac{1}{\sqrt{2}} \frac{r_A + r_O}{r_B + r_O} \le 1.1$$

***ABO_3* Perovskite**



r_A, r_B, r_O : ionic radius

- $t > 1$ — *B atom environment: ample*
- $t = 1$ — *ideal tolerance e.g. $SrTiO_3$*
- $t < 1$ — *B atom environment: scanty*

perovskite oxide	ionic radius *A* ion (Å)	ionic radius *B* ion (Å)	tolerance factor
$BaTiO_3$	1.61	0.61	1.07
$KNbO_3$	1.64	0.64	1.06
$KTaO_3$	1.64	0.64	1.06
$PbTiO_3$	1.49	0.61	1.03
$SrTiO_3$	1.44	0.61	1.00
$NaNbO_3$	1.39	0.64	0.97
$PbZrO_3$	1.49	0.72	0.97
$PbHfO_3$	1.49	0.71	0.97

Ferro-distortive, $q = 0$
(*phase transition at zone center*)

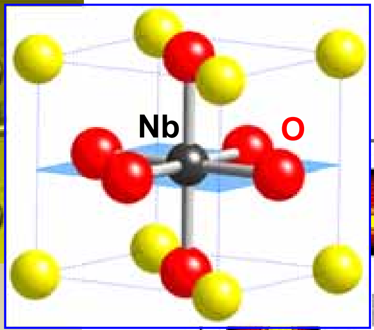
$q \neq 0$ (105 K), $q = 0$ (<0 K)

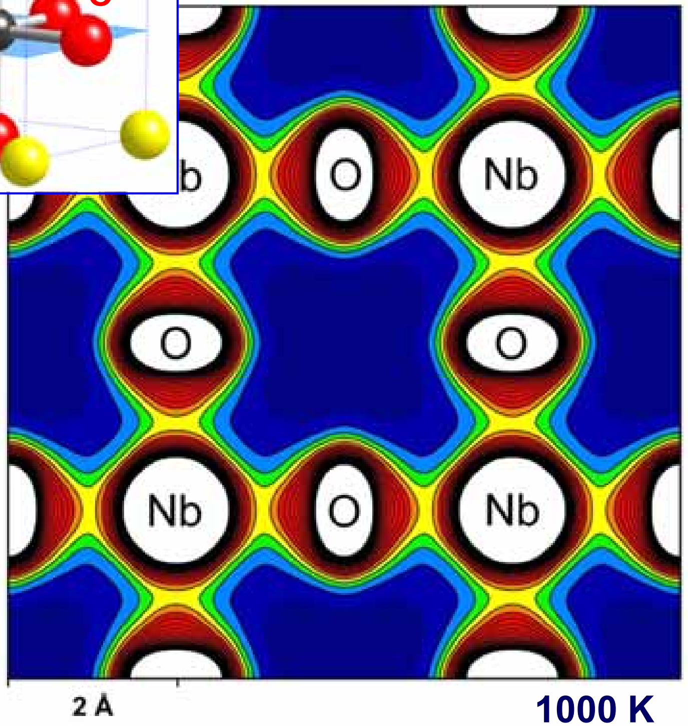
Antiferro-distortive, $q \neq 0$
(*phase transition at zone boundary*)

MEM Charge Density Maps of $NaNbO_3$ & $KNbO_3$ in Cubic Structure on Nb-O Plane

$NaNbO_3$ (T_C = 916 K M_3)

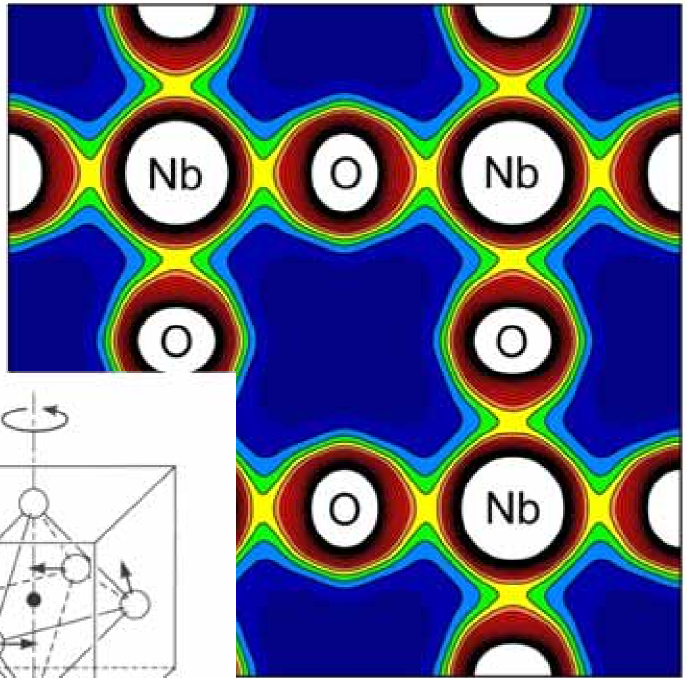
a = 3.94642(1) Å
t = 0.97

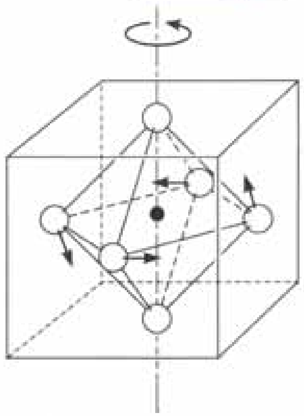




$KNbO_3$ (T_C = 707 K Γ_{15})

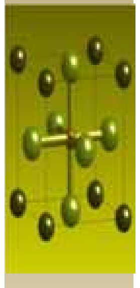
a = 4.03074(1) Å
t = 1.06





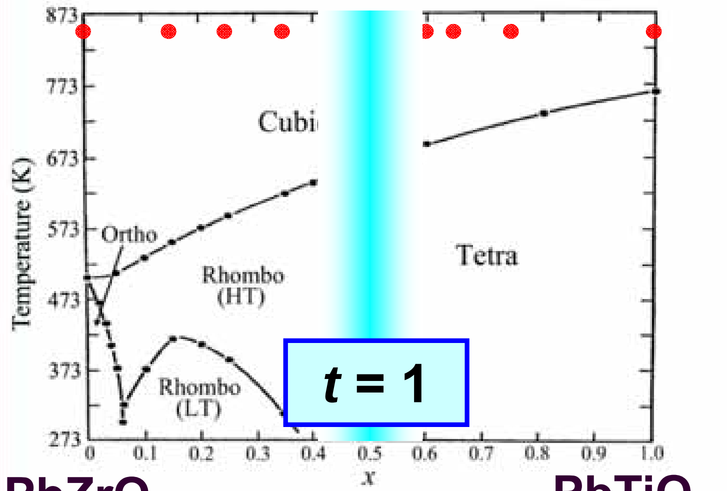
Nb-O plane

Structure parameters of PZT in Cubic Structure at 850 K



PZT

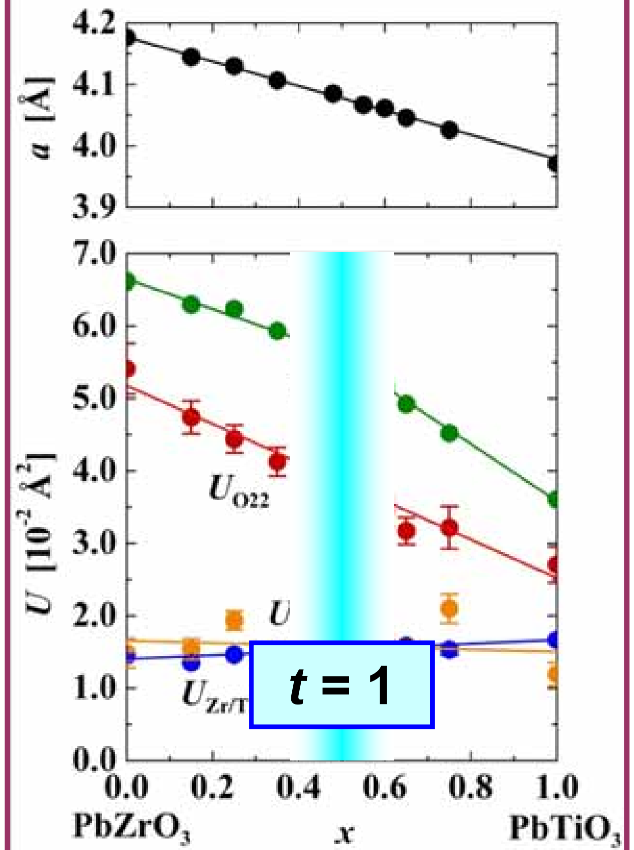
Phase diagram of PZT



$PbZrO_3$ $PbTiO_3$

B. Jaffe *et al.*, "*Piezoelectric Ceramics*" Academic Press, London, (1971) 136

Structure parameter of PZT (*harmonic model*)

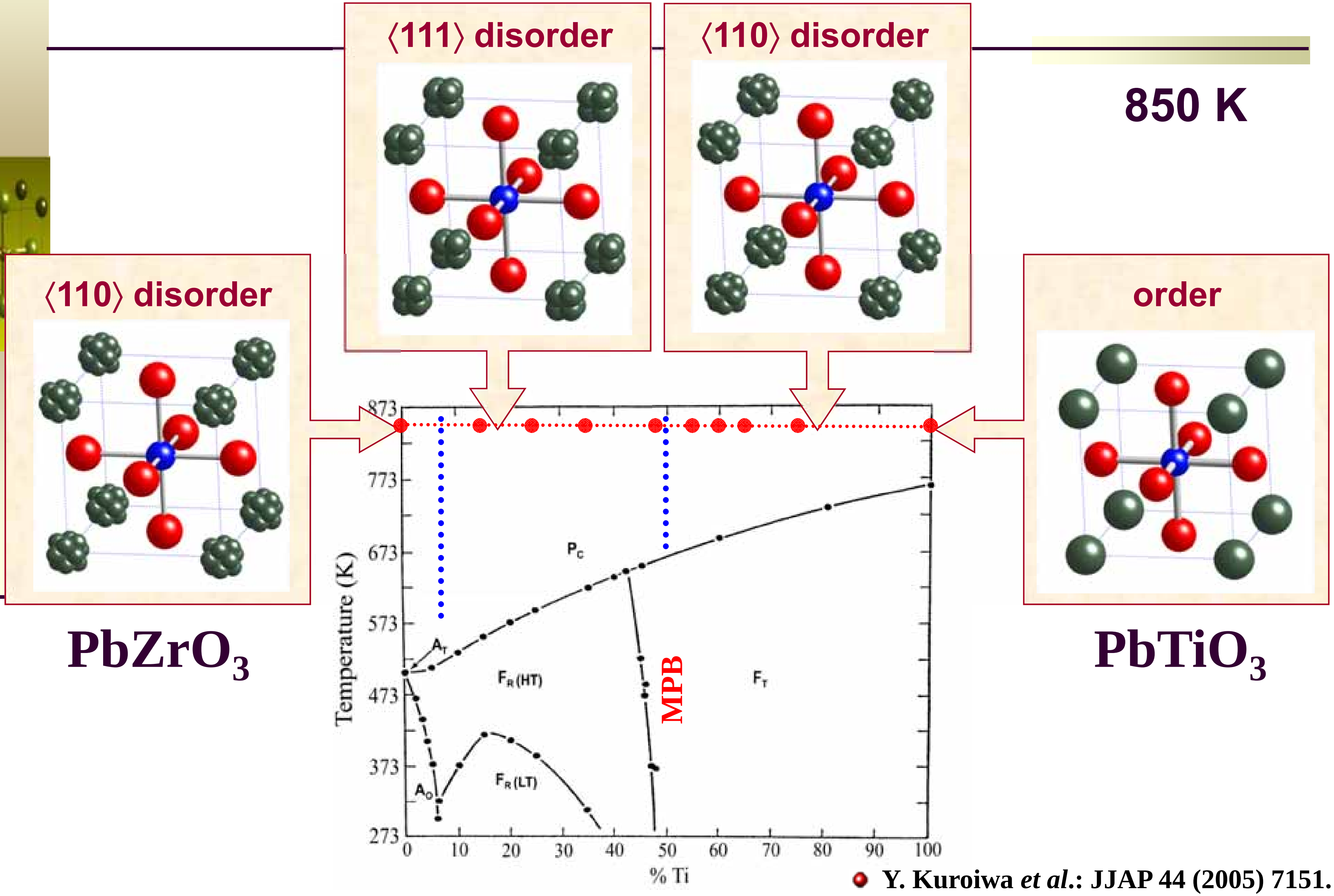


***t* = 0.97** ***t* = 1.03**

- Y. Kuroiwa *et al.*, Jpn. J. Appl. Phys. 44 (2005) 7151

Disordered Structure of PZT in Cubic Phase

850 K



● Y. Kuroiwa *et al.*: JJAP 44 (2005) 7151.

チタン酸バリウムー ニオブ酸カリウムナノ複合セラミックスの界面構造と誘電特性

－元素戦略とMPBエンジニアリング－

－ $BaTiO_3$–$KNbO_3$ ナノ複合材料の結晶構造－

Lead-free Piezoceramics

letters to nature

NATURE | VOL 432 | 4 NOVEMBER 2004 | www.nature.com/nature

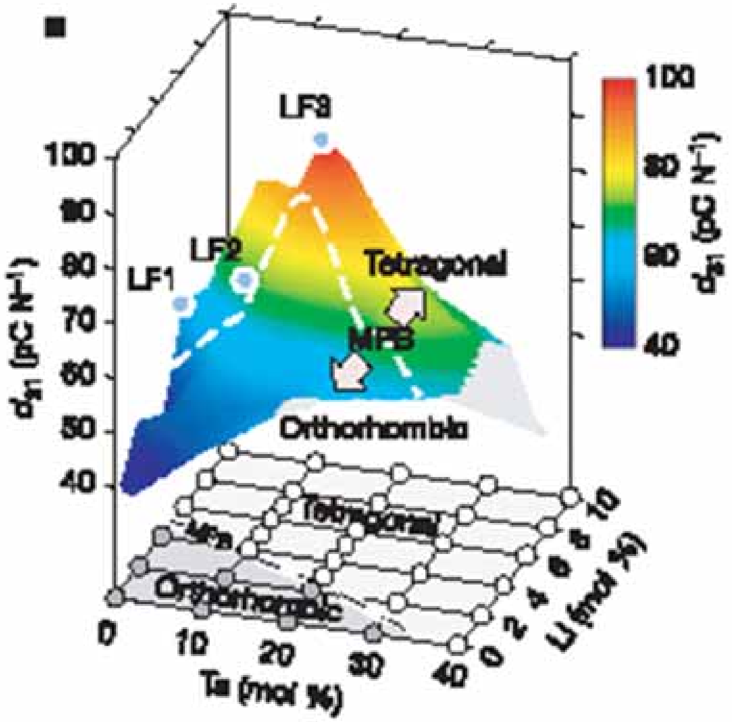
(K, Na)NbO_3-$LiTaO_3$(-$LiSbO_3$)

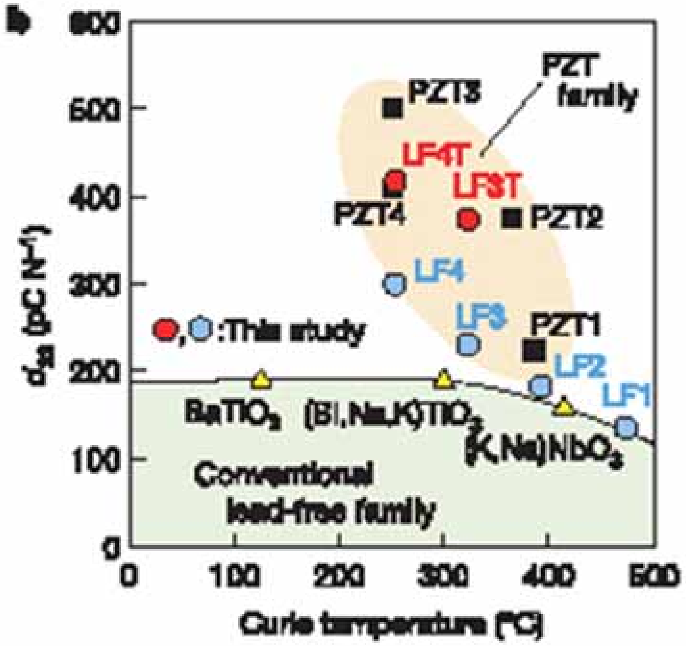
Lead-free piezoceramics

Yasuyoshi Saito[1], Hisaaki Takao[1], Toshihiko Tani[1], Tatsuhiko Nonoyama[2], Kazumasa Takatori[1], Takahiko Homma[1], Toshiatsu Nagaya[2] & Masaya Nakamura[2]

[1] *Toyota Central R&D Laboratories, Inc., Nagakute, Aichi, 480-1192, Japan*
[2] *DENSO Corporation, 1-1, Showa-cho, Kariya, Aichi, 448-8661, Japan*

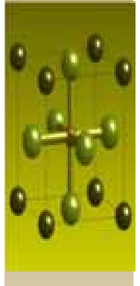
Piezoelectric property		LF4T	PZT4
Curie temperature	T_C (°C)	253	250
Piezoelectric coupling constant	K_p	0.61	0.60
Piezoelectric charge sensor constant	d_{31} (pC N^{-1})	152	170
	d_{33} (pC N^{-1})	416	410
Piezoelectric voltage constant	g_{31} (10^{-3} V m N^{-1})	11.0	8.3
	g_{33} (10^{-3} V m N^{-1})	29.9	20.2
Dielectric constant	$\varepsilon^T_{33}/\varepsilon_0$	1,570	2,300
Normalized strain	S_{max}/E_{max} (pm V^{-1})	750	700





Enhanced Piezoelectric Response of $BaTiO_3$-$KNbO_3$ Composites with Heteroepitaxial Interface

I. Fujii *et al*.: Appl. Phys. Lett. 99 (2011) 202902.



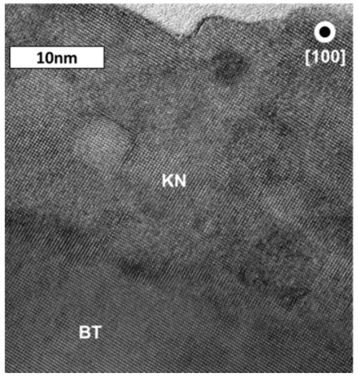
APPLIED PHYSICS LETTERS 99, 202902 (2011)

Enhanced piezoelectric response of $BaTiO_3$–$KNbO_3$ composites

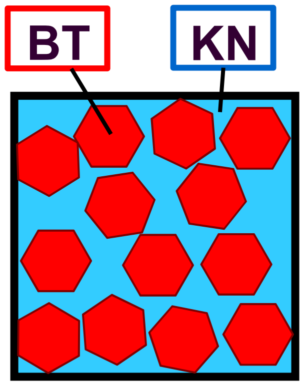
Ichiro Fujii,[1] Shigehito Shimizu,[1] Kenta Yamashita,[1] Kouichi Nakashima,[1] Nobuhiro Kumada,[1] Chikako Moriyoshi,[2] Yoshihiro Kuroiwa,[2] Yoshinori Fujikawa,[3] Daisuke Tanaka,[3] Masahito Furukawa,[3] and Satoshi Wada[1,a)]
[1]*Interdisciplinary Graduate School of Medical and Engineering, University of Yamanashi, Kofu, Yamanashi 400-8510, Japan*
[2]*Department of Physical Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8526, Japan*
[3]*Materials and Process Development Center, TDK Corporation, 570-2 Matsugashita, Minamihatori, Narita, Chiba 286-8588, Japan*

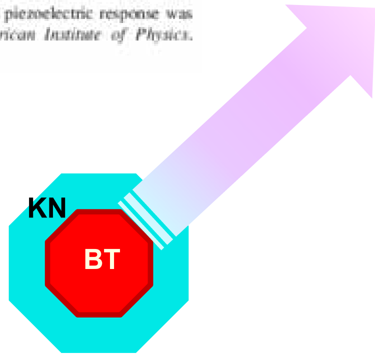
(Received 6 July 2011; accepted 29 October 2011; published online 16 November 2011)

The piezoelectric response of solvothermally synthesized $BaTiO_3$ (BT)–$KNbO_3$ (KN) composites (the nominal BT/KN ratio was 1) with distinct interfaces was investigated. The x-ray diffraction pattern showed two distinct peaks began to merge into a singular broad peak at a two-theta position between (200) and (002) tetragonal-related peaks of BT. The transmission electron microscopy observation showed a heteroepitaxial interface region between BT single-crystal particles and deposited KN crystals. The large-field piezoelectric constant was 136pC/N, which was three times larger than that of a sintered 0.5BT-0.5KN composite. The enhanced piezoelectric response was attributed to the strained epitaxial interface region. © *2011 American Institute of Physics.* [doi:10.1063/1.3662397]

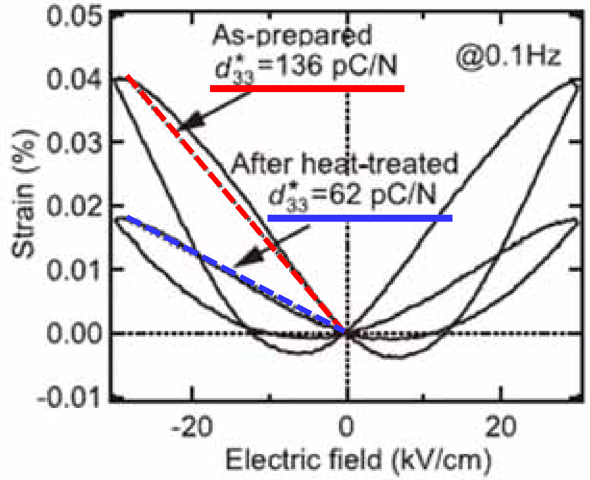


Artificial Interface between Polar Nano-BT Region and KN





KN on BT
BT: nano-particle ϕ300 nm



BT-KN Composites with Heteroepitaxial Interface (HE I/F)

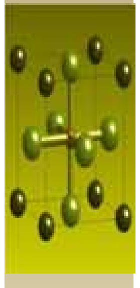
☺ d_{33} = 136 pC/N (w HE I/F),

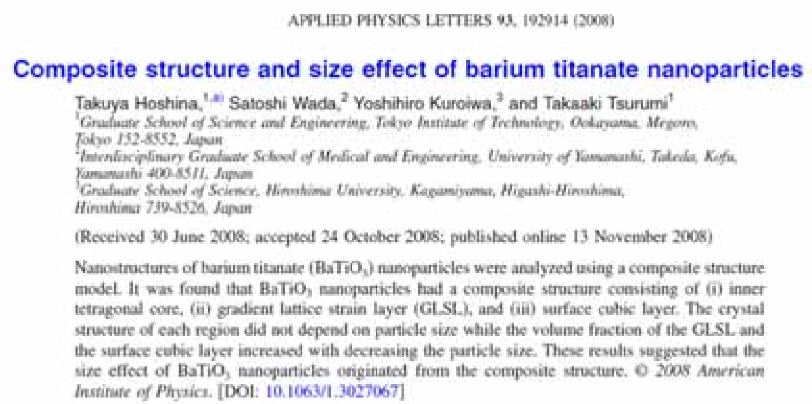
☹ d_{33} = 40 pC/N (w/o HE I/F)

Strain vs. Electric-field Curves

Size Effect of $BaTiO_3$ Nanoparticles with Gradient Lattice Strain Layer (GLSL)

T. Hoshina *et al.* : Appl. Phys. Lett. 93 (2008) 192914.





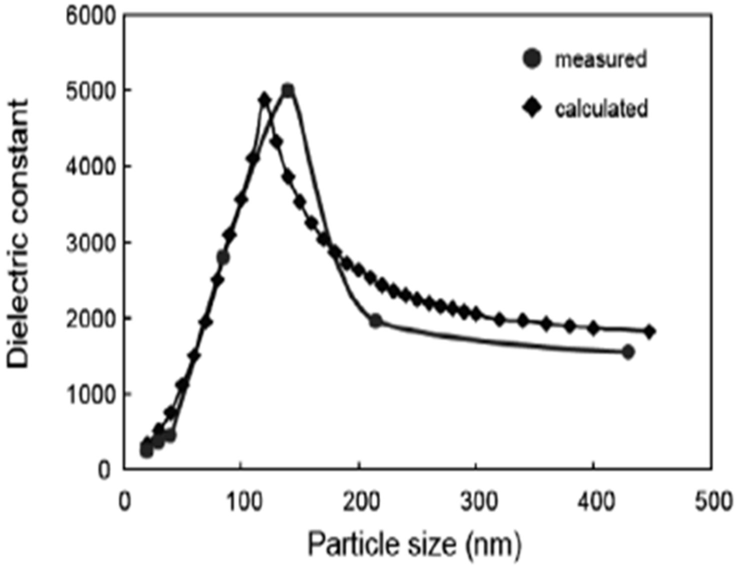
APPLIED PHYSICS LETTERS 93, 192914 (2008)

Composite structure and size effect of barium titanate nanoparticles

Takuya Hoshina,[1,a)] Satoshi Wada,[2] Yoshihiro Kuroiwa,[3] and Takaaki Tsurumi[1]
[1]*Graduate School of Science and Engineering, Tokyo Institute of Technology, Ookayama, Meguro, Tokyo 152-8552, Japan*
[2]*Interdisciplinary Graduate School of Medical and Engineering, University of Yamanashi, Takeda, Kofu, Yamanashi 400-8511, Japan*
[3]*Graduate School of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8526, Japan*

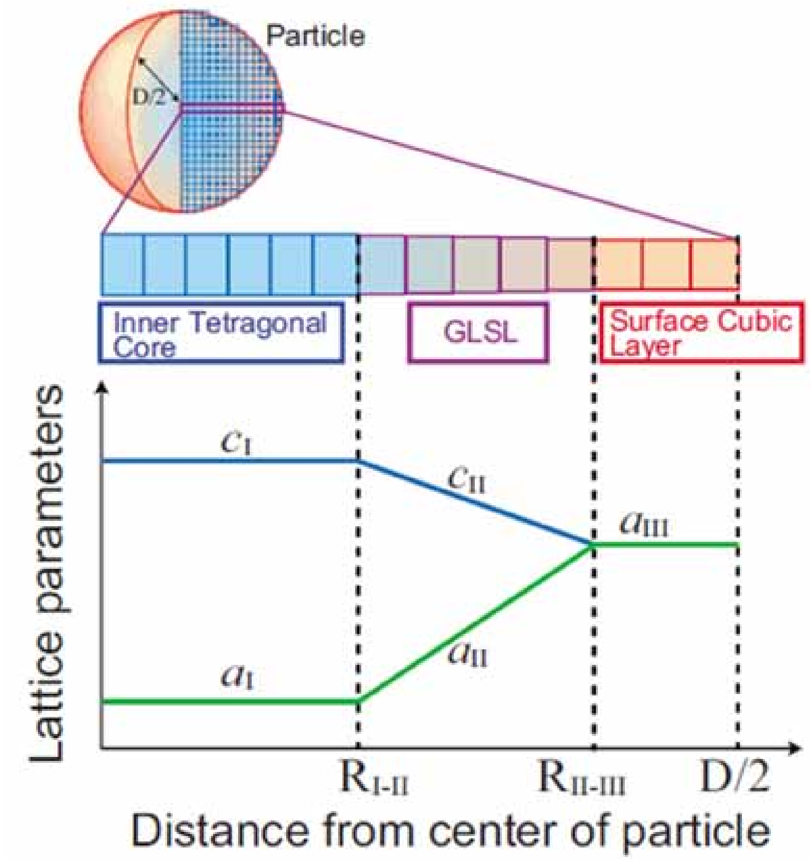
(Received 30 June 2008; accepted 24 October 2008; published online 13 November 2008)

Nanostructures of barium titanate ($BaTiO_3$) nanoparticles were analyzed using a composite structure model. It was found that $BaTiO_3$ nanoparticles had a composite structure consisting of (i) inner tetragonal core, (ii) gradient lattice strain layer (GLSL), and (iii) surface cubic layer. The crystal structure of each region did not depend on particle size while the volume fraction of the GLSL and the surface cubic layer increased with decreasing the particle size. These results suggested that the size effect of $BaTiO_3$ nanoparticles originated from the composite structure. © 2008 *American Institute of Physics*. [DOI: 10.1063/1.3027067]



T. Hoshina : 日本結晶学会誌 51 (2009) 300.

Particle-size Dependence of Dielectric Constant

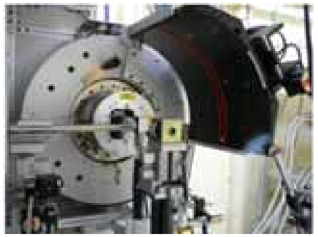


Composite Structure Model of $BaTiO_3$ Nanoparticles

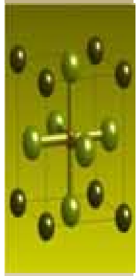
Experimental

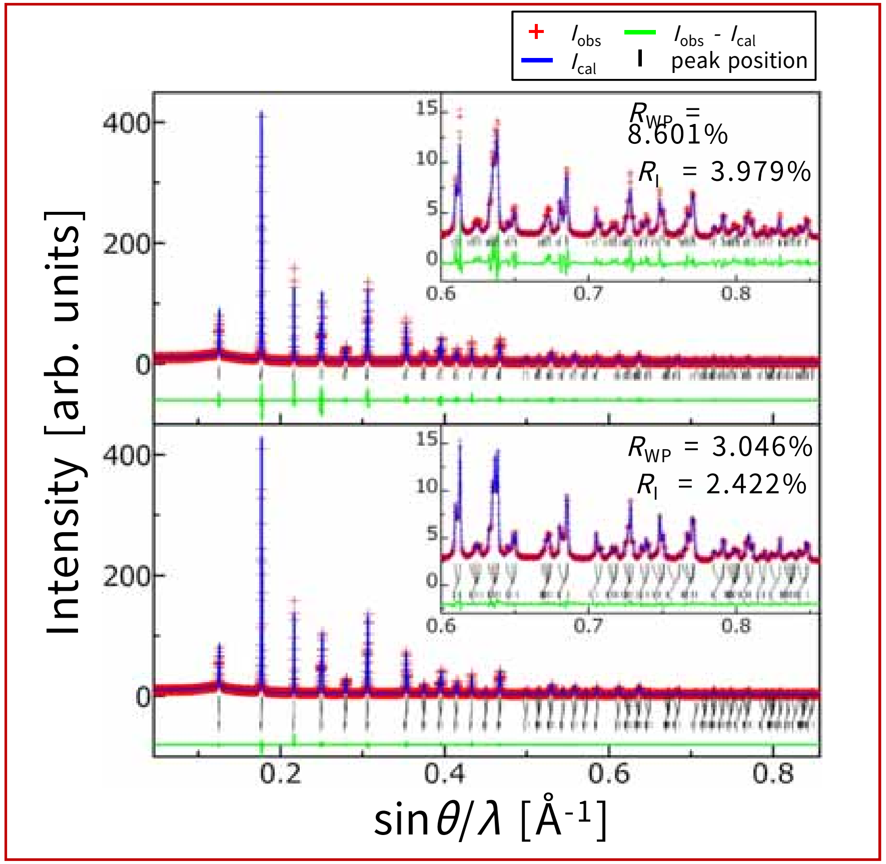
- Synthesizing $BaTiO_3$-$KNbO_3$ nano-composite ceramics with heteroepitaxial interface
  - **Solvothermal method**
    KOH + K_2CO_3 + Nb_2O_5 +
    BT03 (ϕ300 nm), EtOH
    20 hrs @230℃
  - **Dielectric constant**
    2 x 2 x 0.5 mm^3
    1 MHz (HP4294A) @RT

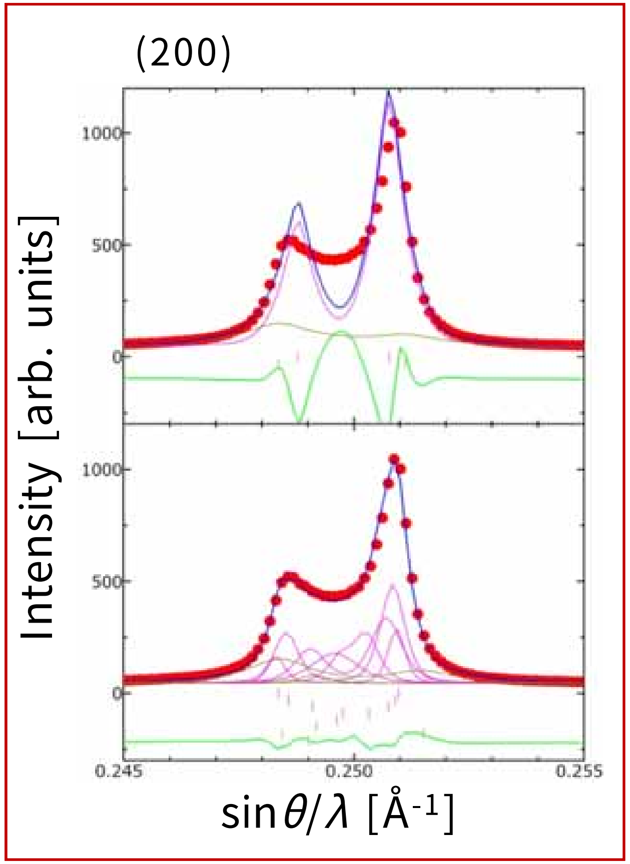
- Characterizing crystal structures which govern dielectric properties
  - **SR powder diffraction**
    SPring-8 BL02B2
    0.67 Å (18.5 keV) @RT
  - **Rietveld analyses**
    9 samples：KN/BT = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 1.0



Rietveld Profile Fitting for BT-0.5KN

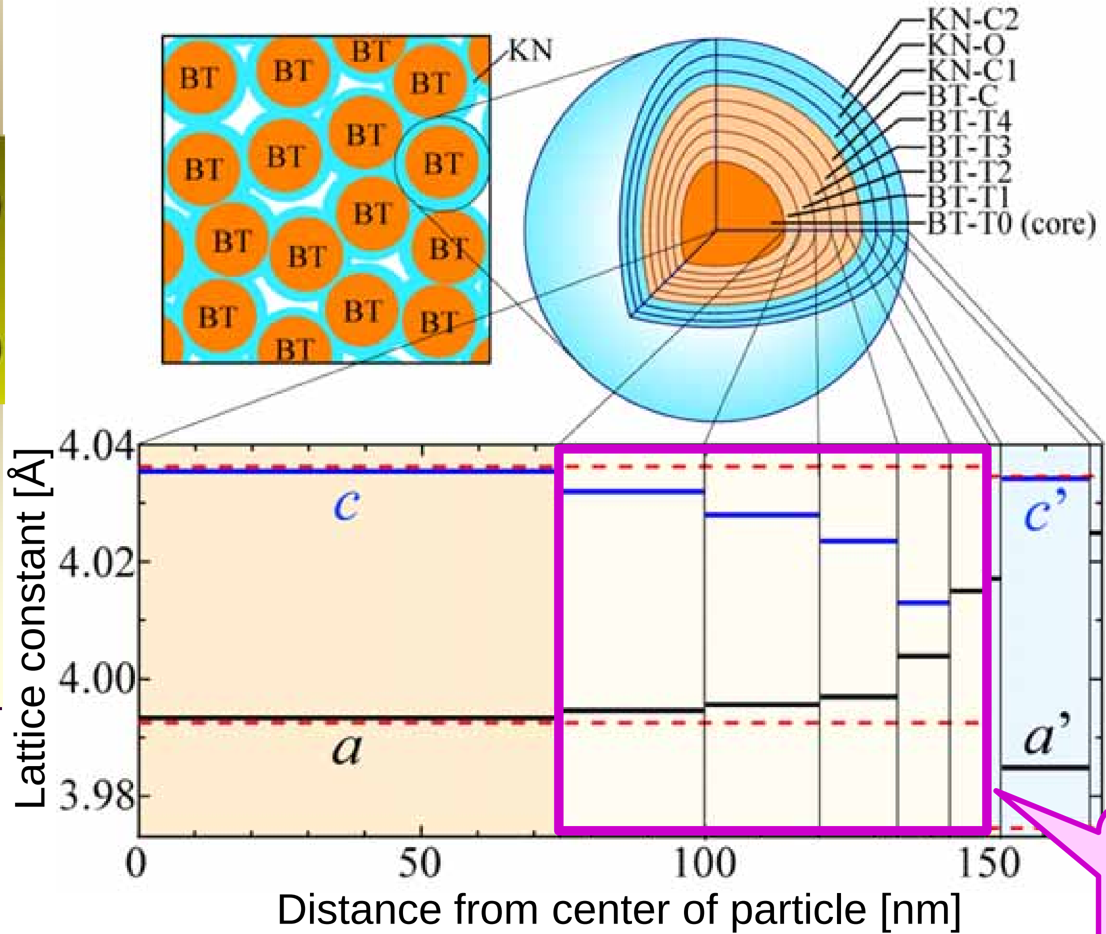




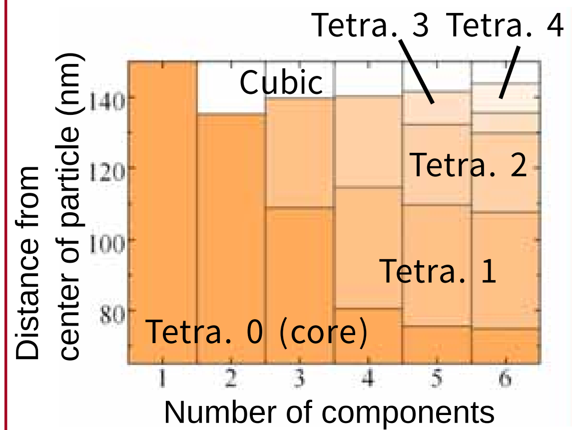


- Upper: BT(tetra) + KN(ortho)
- Lower: BT(5 tetra with different *c*/*a* and cubic) + KN (ortho + 2 cubic with different *a*)

Core/Multi-Shell Structure Model of BT-0.5KN



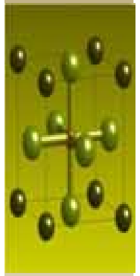
Variation of Lattice Constants in BT-0.5KN



Validity of Six Components in Analyzing BT Structure of BT-KN Composites

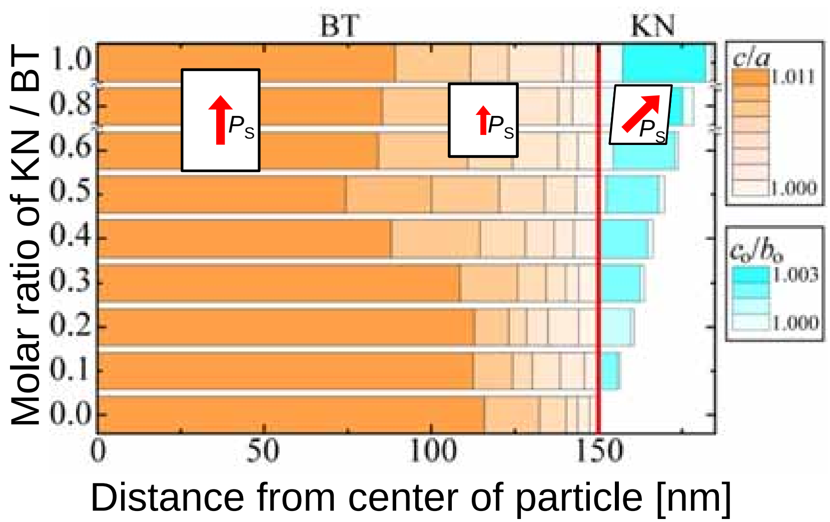
BT multi-shells with less *c/a* than BT core

$V^{BT}_{multi\text{-}shell}$ = 87.57%

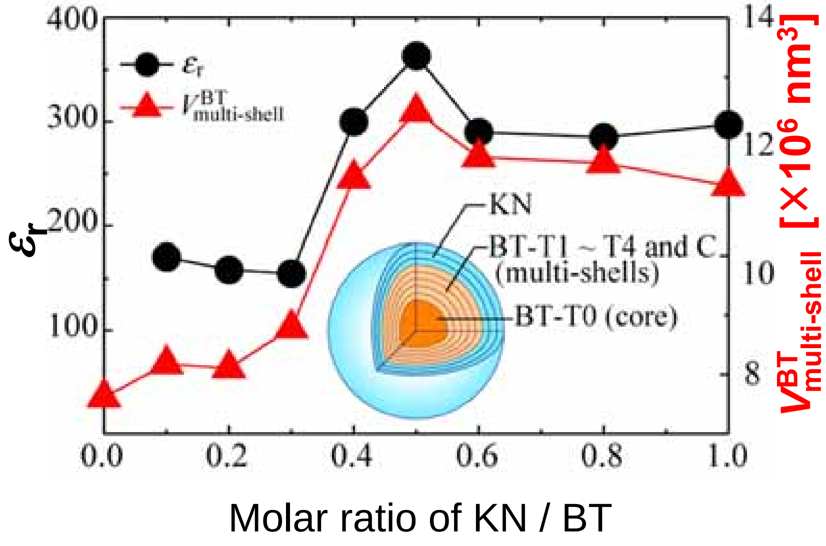


Relationship between Relative Permittivity and Structural Characteristics

Variation of *c*/*a* of BT and c_o/b_o of KN



Variations in ε_r and $V_{BT\text{-}T1 \sim T4}$



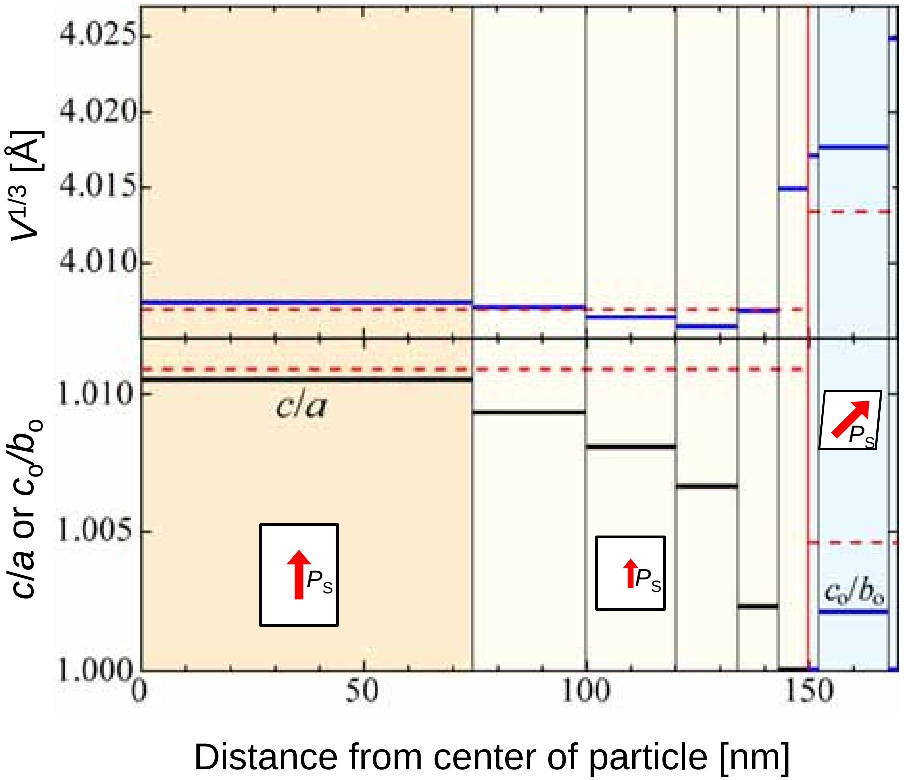
Bulk Crystal

BT(tetra.) : *a* = 3.9933 Å, *c* = 4.0364 Å, $V^{1/3}$ = 4.0076 Å

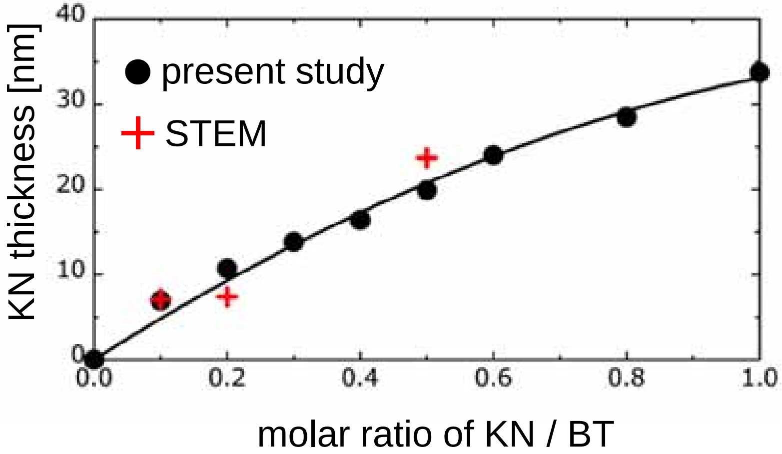
KN(ortho.) : *a* = 3.967 Å, *b'* = *c'* = 4.035 Å, *a* = 90.22º, $V^{1/3}$ = 4.0151 Å (primitive)

The volume of the distorted interface region of BT and the dielectric property show a similar trend in the variation of the KN/BT molar ratio, which suggests that the electrically soft interface between KN and BT governs the dielectric properties of the KN/BT composite ceramics.

Structural Characteristics of BT-KN Composites



Variation of Unit Cell Volume and *c/a* ratio in BT-0.5KN



Thickness of KN Layer estimated by Rietveld Refinement and STEM Observation

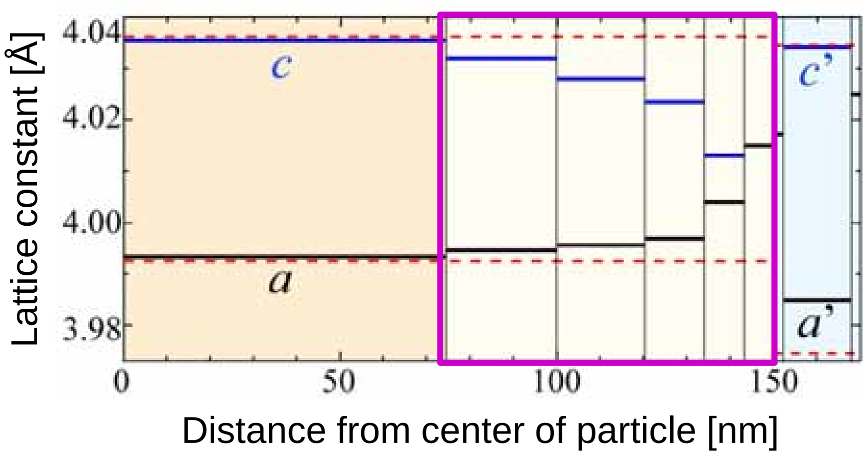
まとめ

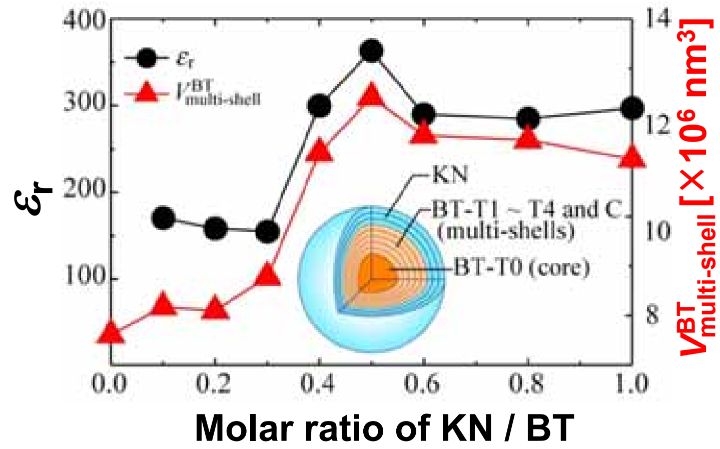
―誘電物性と結晶構造の一対一対応研究の重要性―

BT-KNナノ複合セラミックスの界面構造と誘電特性　まとめ

- BT−KNナノ複合セラミックスの界面構造を解析し，core/multi−shell構造モデルを提案した.
- BTの界面領域がナノ複合セラミックスの誘電特性と密接な関係にある.

- **複雑な物質系に対しては，誘電物性と結晶構造を一対一に対応させた議論が必要.**





E. Magome *et al* : Jpn. J. Appl. Phys. 51 (No.9) (2012) in press.