Phonon Workshop 2007, Cracow, Poland 2007.12.5-8 Invited Lecture

TOKAI UNIVERSITY

Phonons in $SrTiO_3$ analyzed by difference bond-length spectrum

Wilfried Wunderlich,
Tokai University, Fac.Engr., Dept. Material Science,
259-1292 Kanagawa-ken, Japan

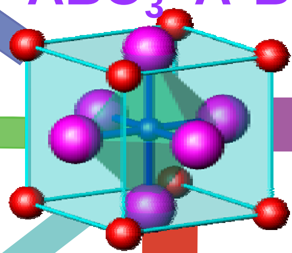
- o Motivation: Functional Nanomaterials
- o New ideas about phonons in $SrTiO_3$
- o Nano-layered Interfaces $SrTiO_3$-SrO, ..

http://www.angelfire.com/wi/wunder/index.html

Nonlinear solid-state physics effects

Piezoelectric
$Pb(ZrTi)O_3$ (PZT)

Perovskite
ABO_3 $A^+BO_6^-$

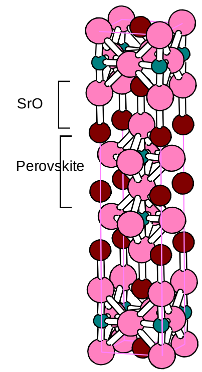


Colossal Dielectric Constant
$(BaSr)TiO_3$ $\varepsilon > 10000$

Giant-Magnetic Resistance
$(LaSr)MnO_3$ (LSM)

Superconductor
Bi2212 T_C=120K

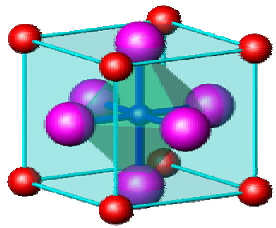
$(SrTiO_3)SrO$
Thermoelectric



ZT= 0.7 (1000K)

H. Ohta, S.Ohta, K. Koumoto
Proc. ICT (2004)

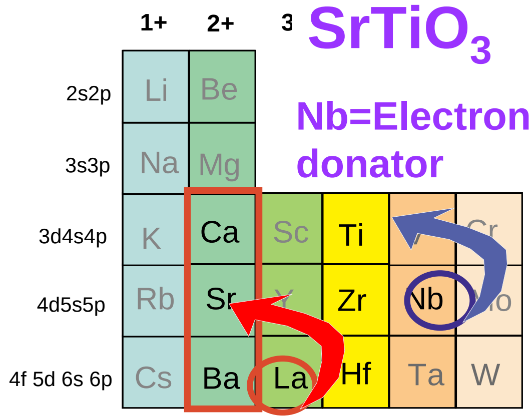
n-Doping of $SrTiO_3$



ABO_3

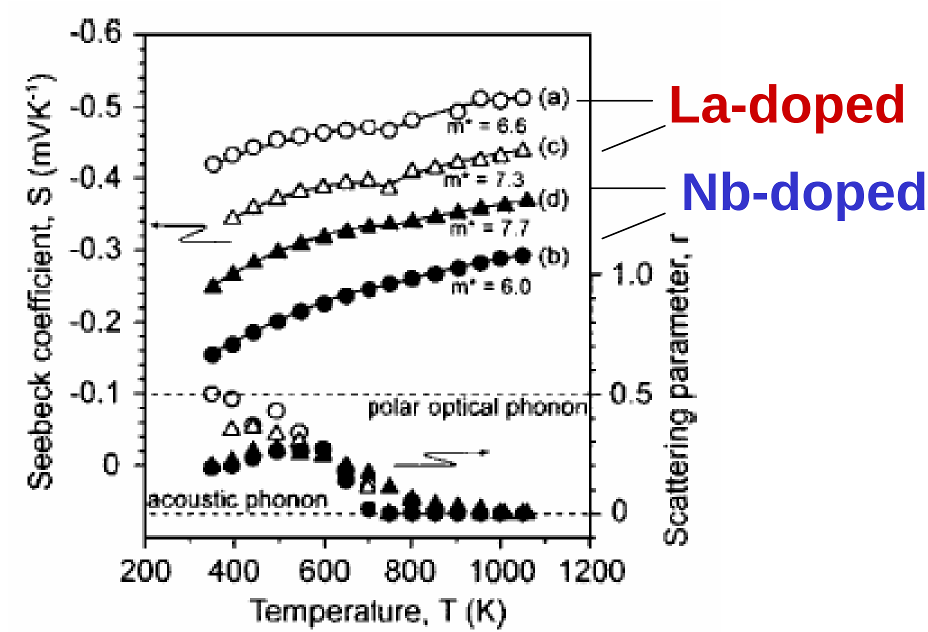
$SrTiO_3$

Nb=Electron donator



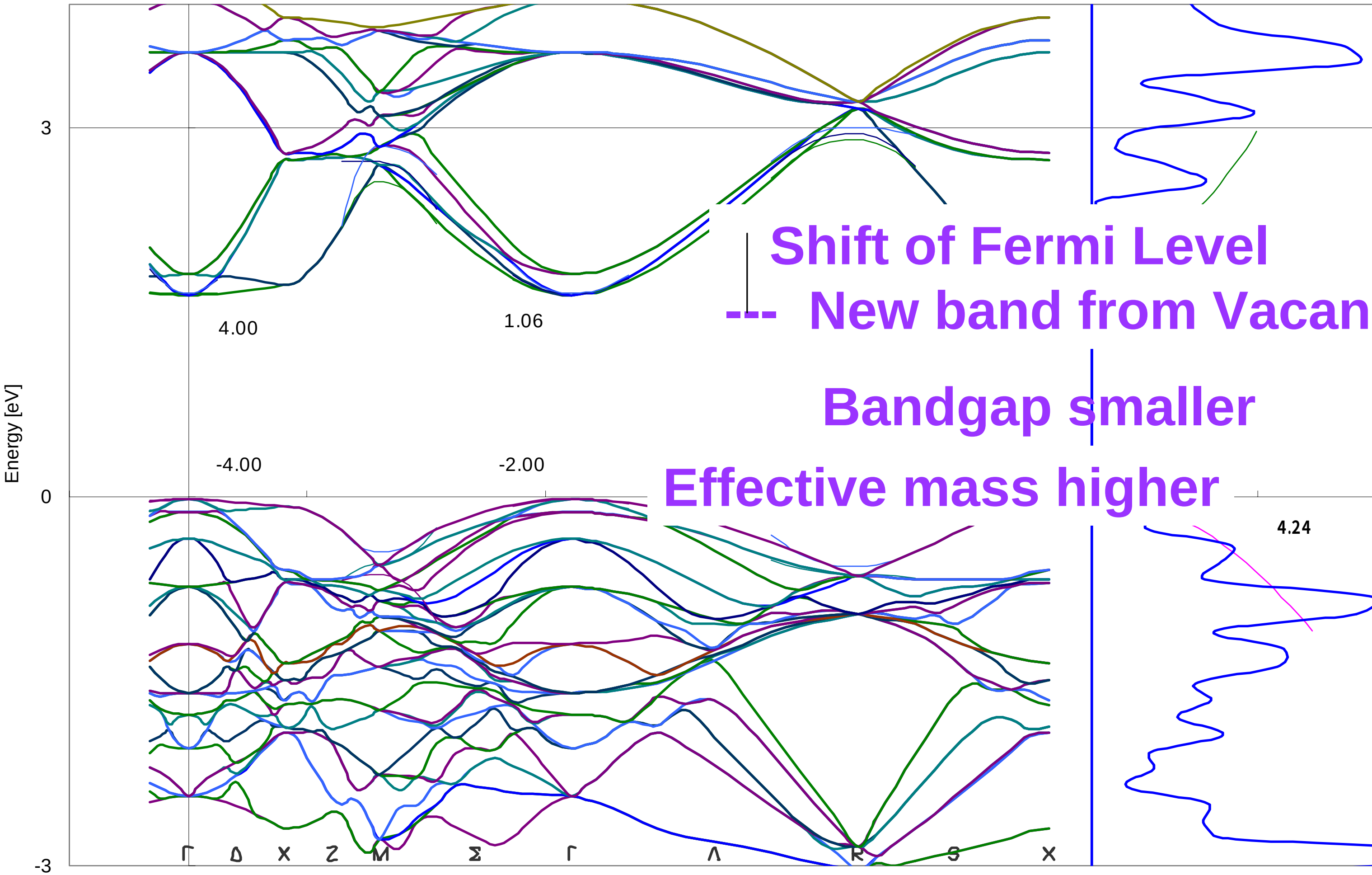
A-side doping

B-side doping



Experiment: H. Ohta, S.Ohta, K. Koumoto
J.App.Phys. 97 (2005) 034106

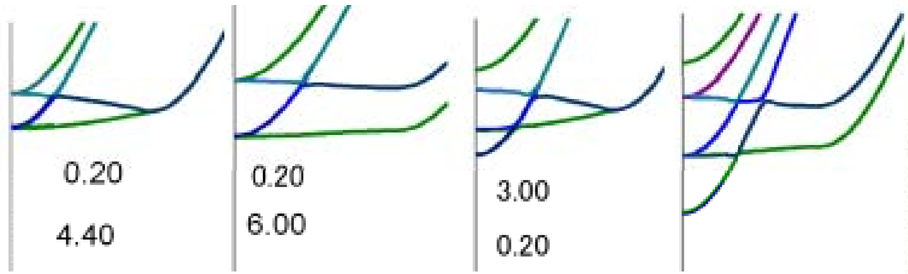
Effective mass of Nb@ $SrTiO_3$



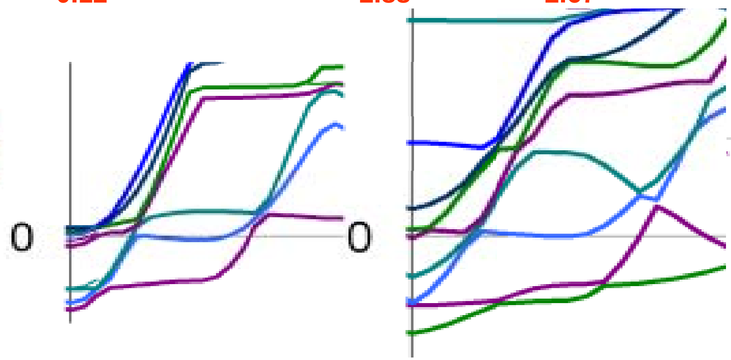
W.Wunderlich, H.Ohta, K.Koumoto, cond-mat/0510013

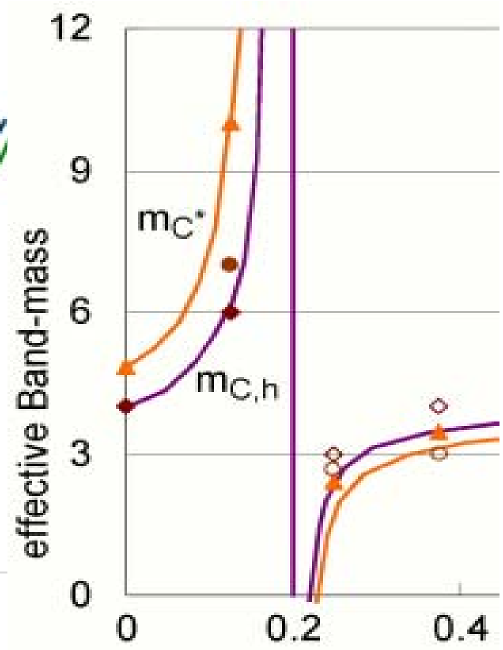
Nb-doped $SrTiO_3$

$Nb_{0.12}$ $Nb_{0.24}$ $Nb_{0.36}$ $Nb_{0.5}$



$Nb_{0.12}$-doped $SrTiO_{2.88}$ /$SrTiO_{2.67}$





-> Effective mass > 12
more two time larger
than pure $SrTiO_3$

Result:
Insulator-Metal-Transition

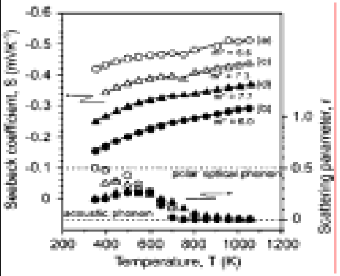
-> 1.Guideline
very narrow concentration range
for best performance

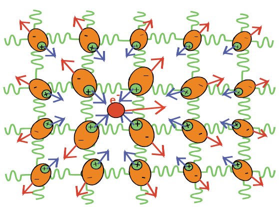
W.Wunderlich, H.Ohta, K.Koumoto, cond-mat/0510013

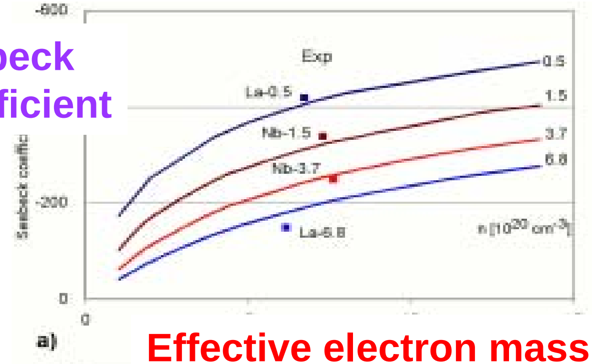
TE properties Calculation on atomistic level

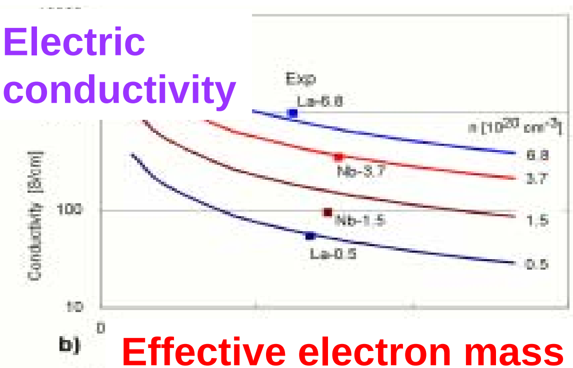
Experiment: H. Ohta, S.Ohta, K. Koumoto J.App.Phys. 97 (2005) 034106

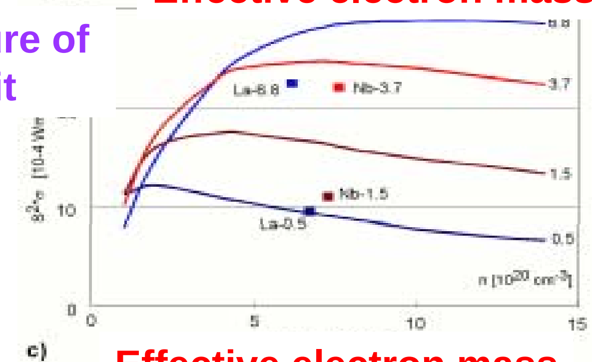
Theory: C. B. Vining: J. Appl. Phys. 69 (1991) 331

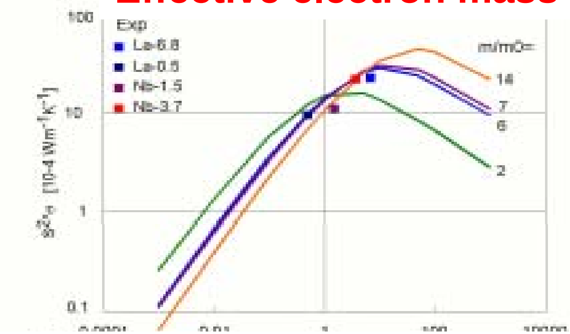








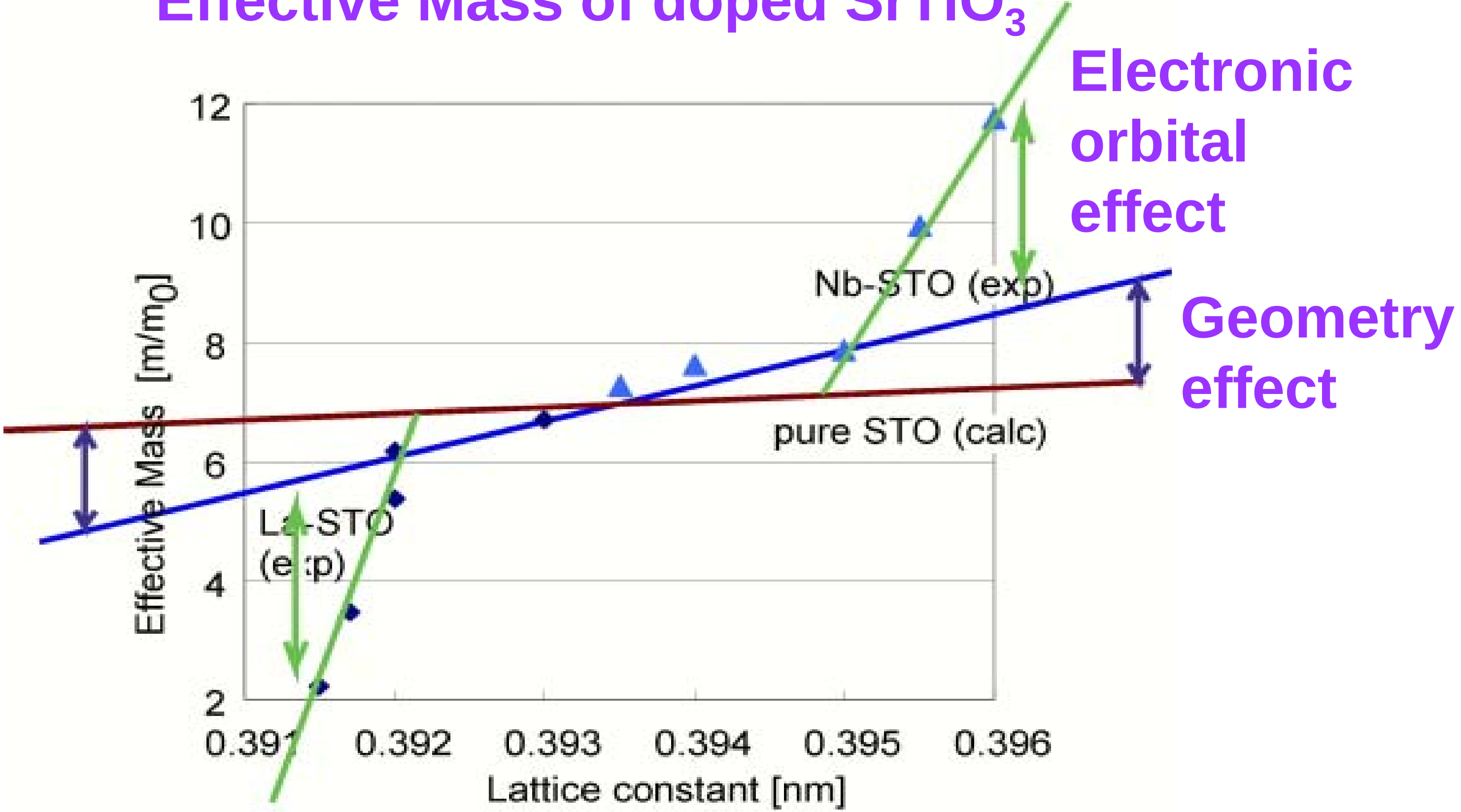




2.Guideline: Search for materials with large effective electron mass

W.Wunderlich, K.Koumoto, Int.J. Mat. Res. 97 (2006) 5 657-662

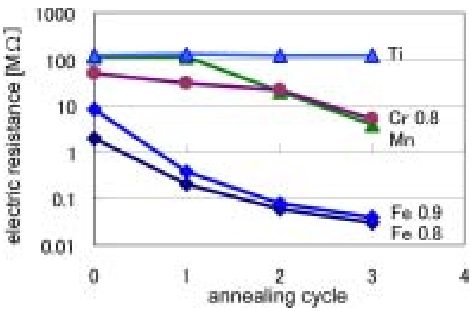
Effective Mass of doped $SrTiO_3$

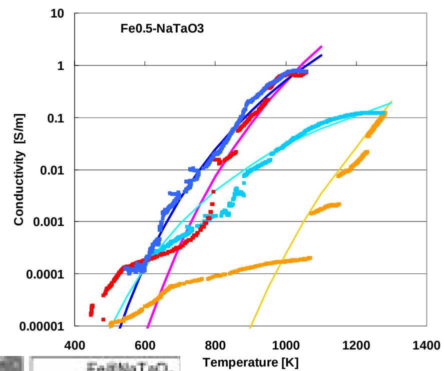


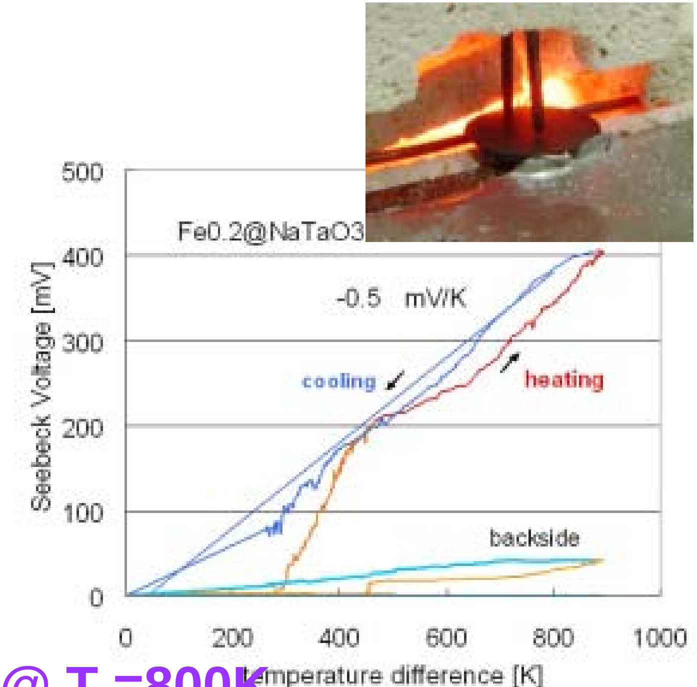
3.Guideline: Increase charge density on B-side namely Ti-Octahedron

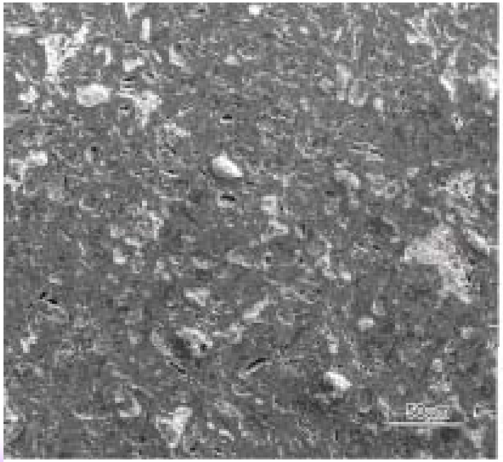
W.Wunderlich, H.Ohta, K.Koumoto, cond-mat/0510013

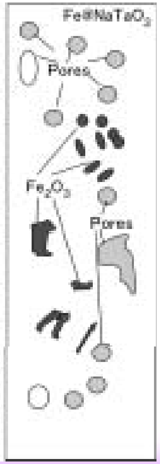
Material with large effective mass: $NaTaO_3$ $(+Fe_2O_3)$











σ=1S/m @ T =800K

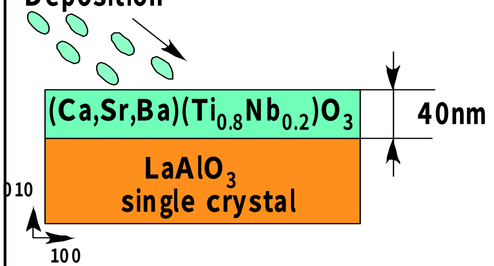
S=400mV/K @ ΔT =800K

W.Wunderlich, T.Soga, Proc.Jap.Thermoel.Soc. (2007)

Thermoelectric Phase Diagram

Figure of merit $Z = S^2\sigma/\kappa$
Seebeck coefficient S
Electric conductivity σ
Thermal conductivity κ

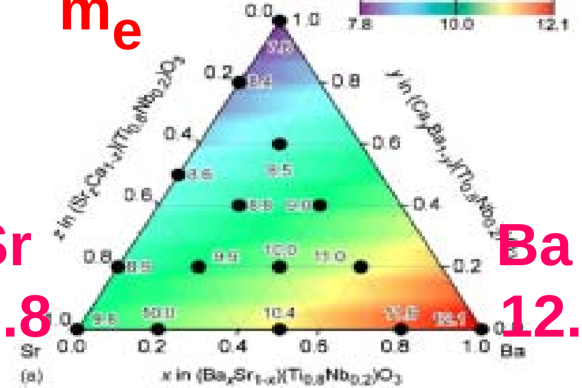
PLD Pulsed Laser Deposition



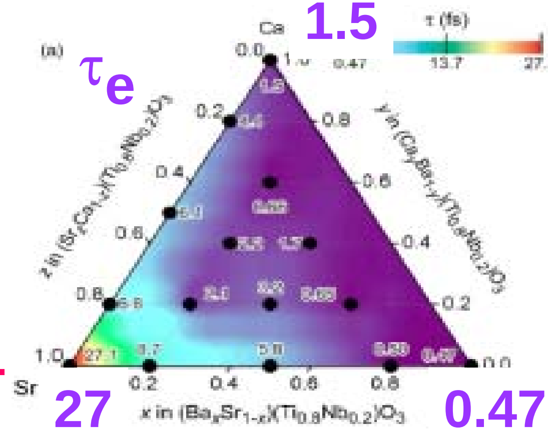
Epitaxial Orientation Relationsship
(001)[100]$_{\text{Thin Film}}$ || (001)[100] $_{\text{Substrate}}$

σ, μ, S, κ → m_e, τ_e, n_e, τ_p

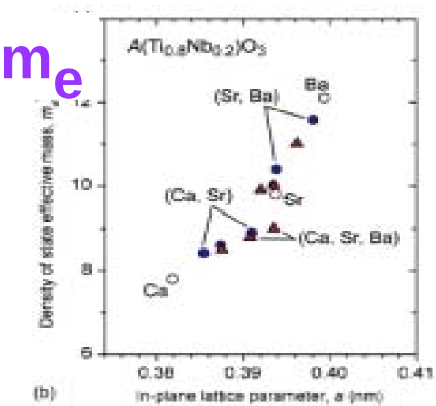
m_e Ca 7.8, Sr 9.8, Ba 12.1



τ_e 1.5, 27, 0.47

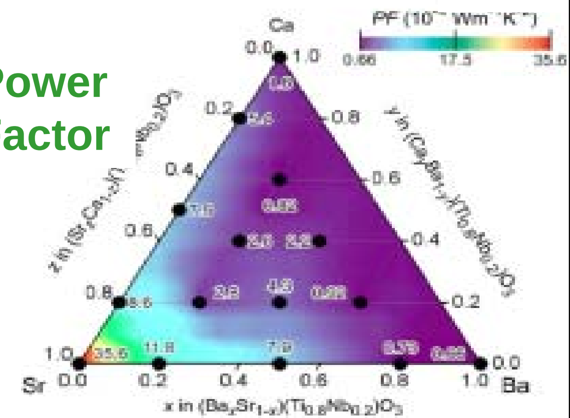


m_e



Lattice constant

Power Factor



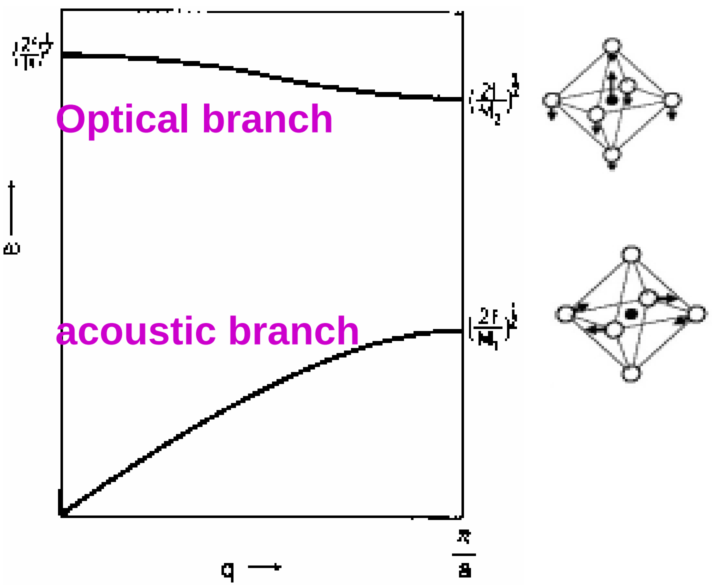
Yamamoto, Ohta, Koumoto., Appl. Phys. Lett. 90, 072101 (2007)

Phonon calculations

and Comparison with experiments

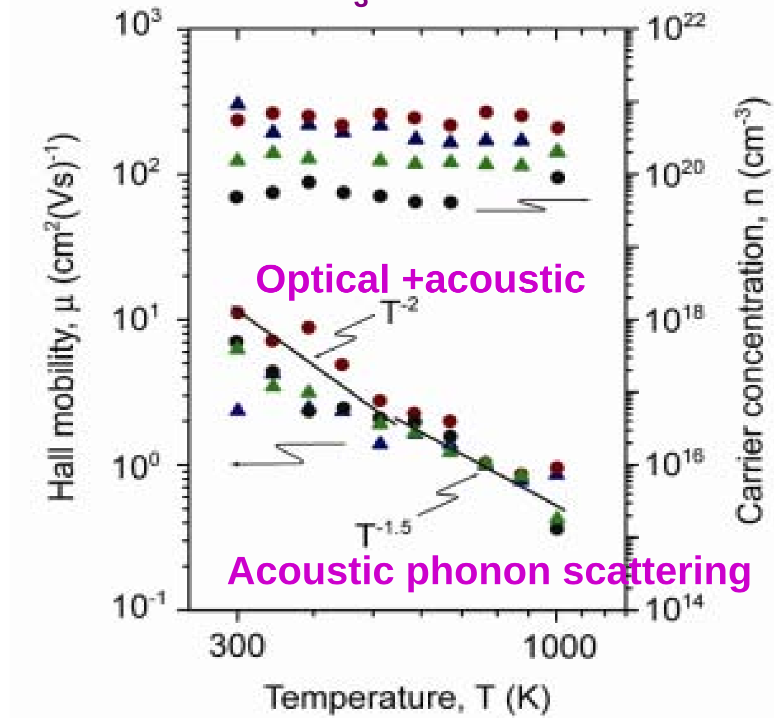
$$k = \frac{1}{3} C\, v\, l$$

Specific heat — Sound velocity — Phonon *mfp*



$SrTiO_3$-6%Nb

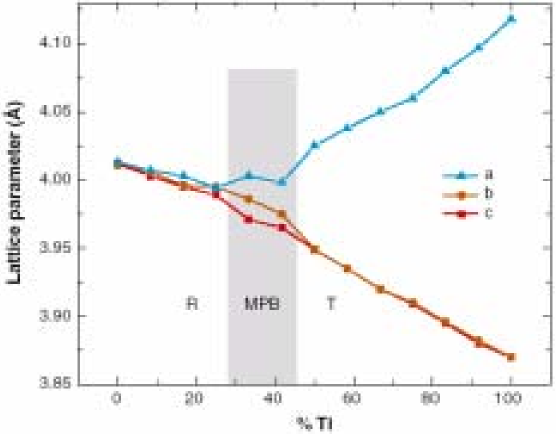
$SrTiO_3$-6%La

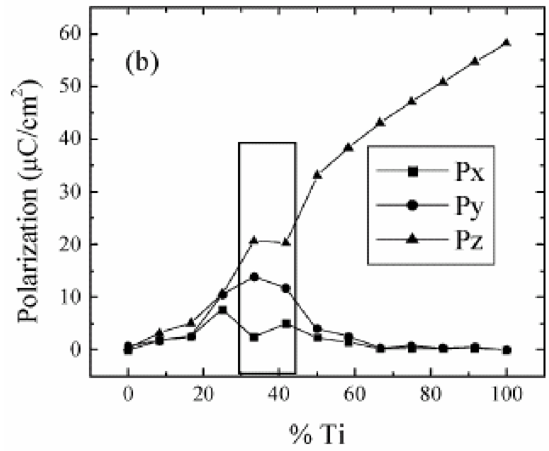


H. Ohta, S.Ohta, K. Koumoto J.App.Phys. 97 (2005) 034106

Soft Phonon modes indicate phase transition

$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT),

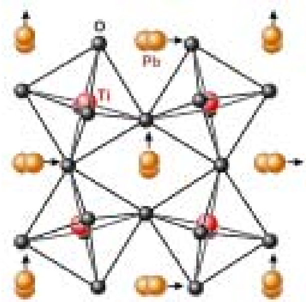




Rhombohedral tetragonal

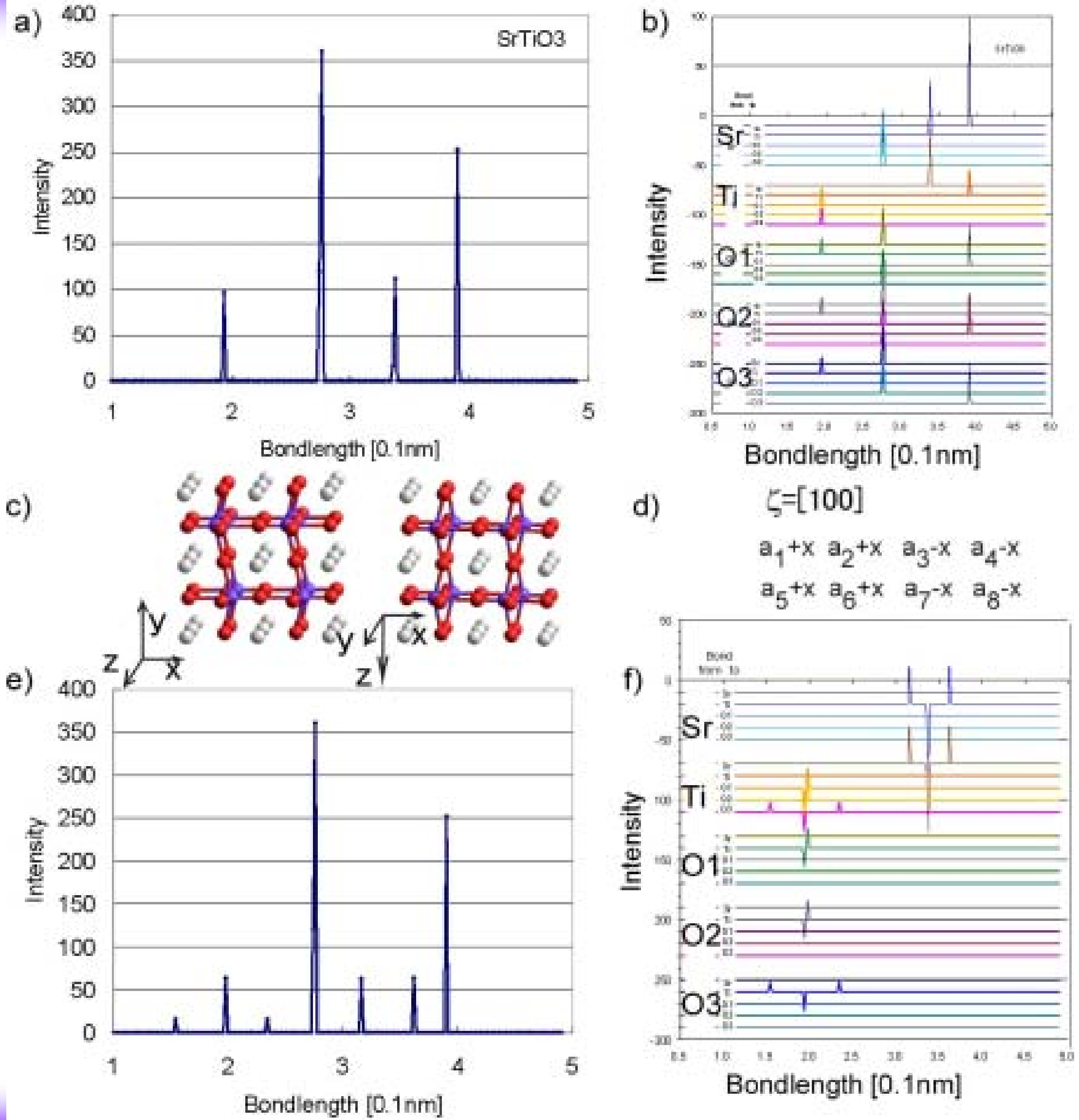
MPB: morphotropic phase boundary

Large Polarization mode



Simon R.Phillpot, S.Sinnott, Ann.Rev.Mat Sci.37, 239-70 (2007)

Asthagiri, Wu et.al. Ferroelectrics 333, 69-78 (2006).



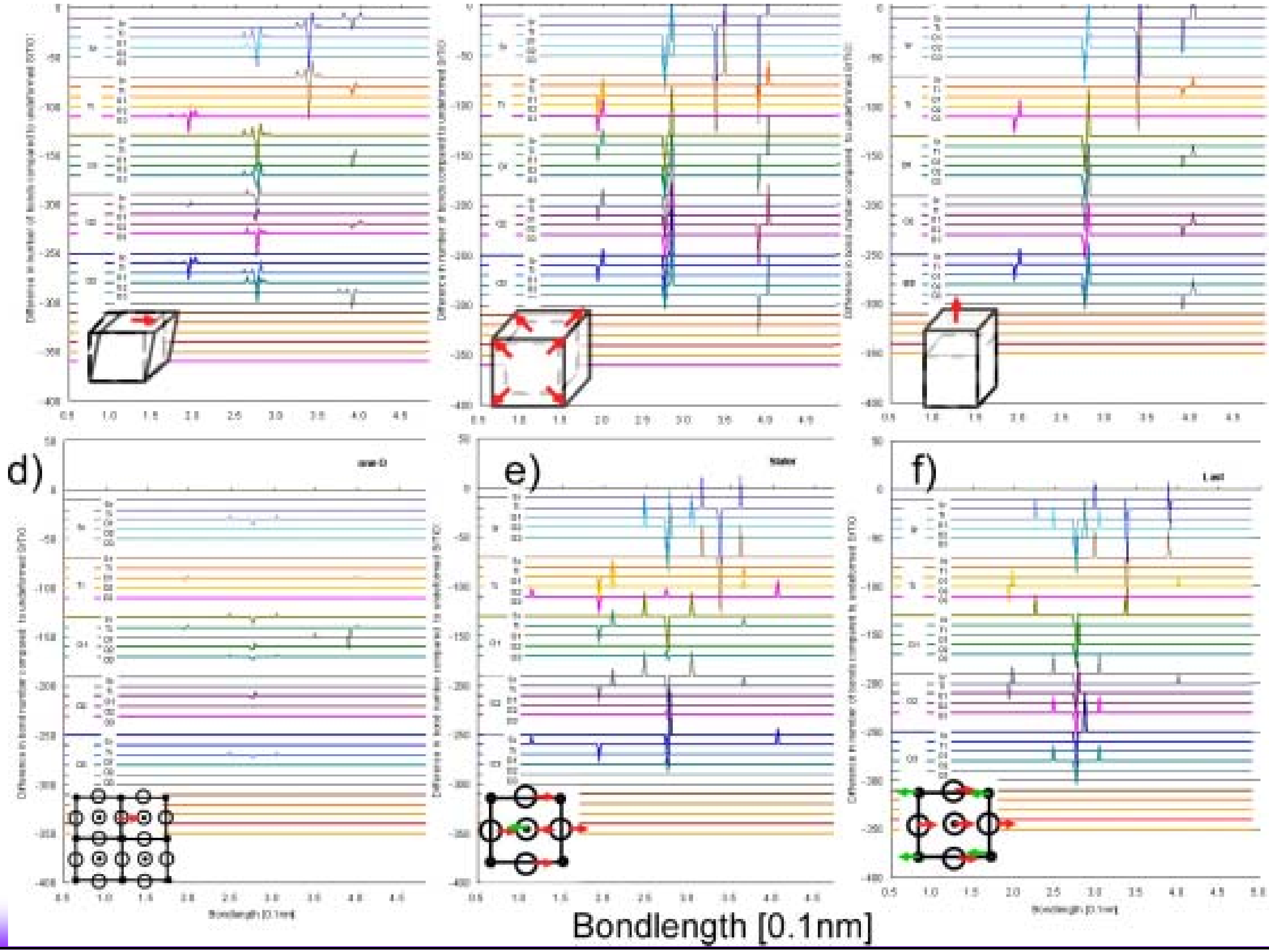
Bond length spectrum

= Radial distribution function

= pair correlation function

W.Wunderlich,
arxiv.org/abs/0711.0567

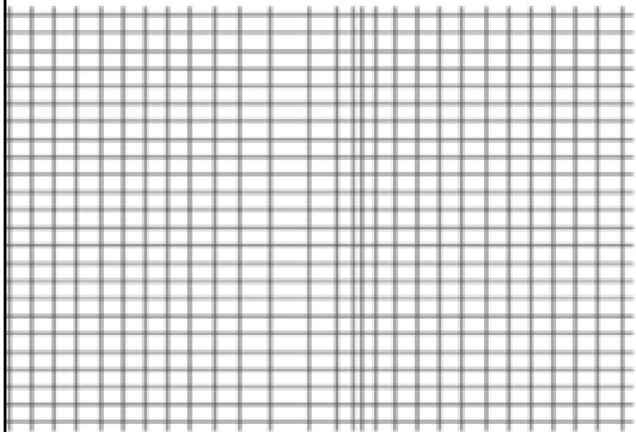
Bondlength spectrum for distortions and phonons



Waves in solids

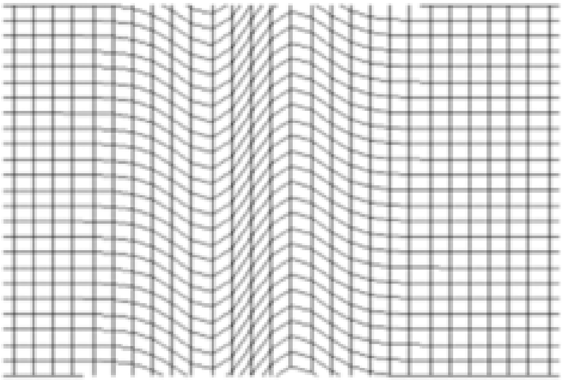
Earth quake waves

Longitudinal wave

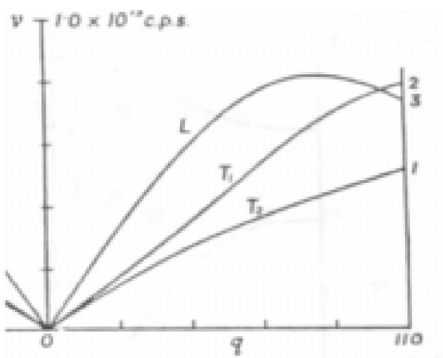


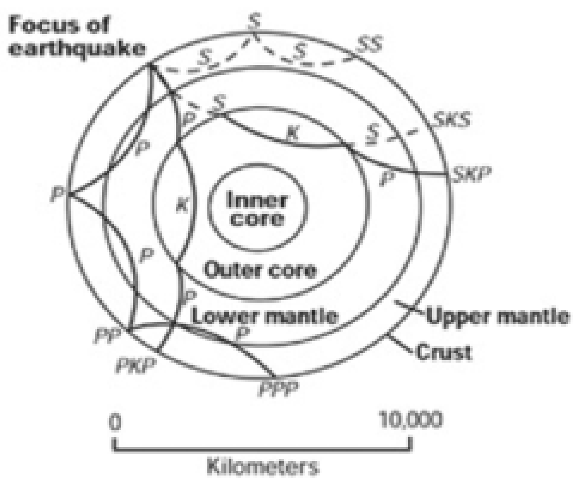
P-wave,
5-7km/s=
15000km/h

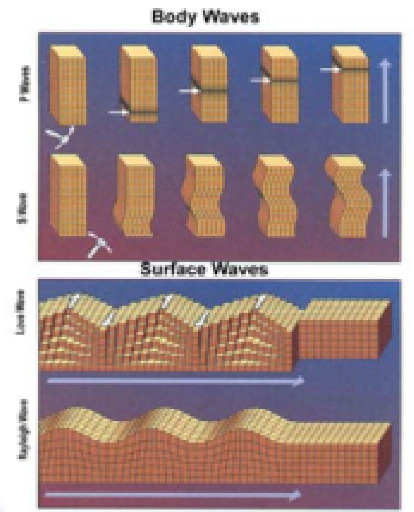
Transverse wave



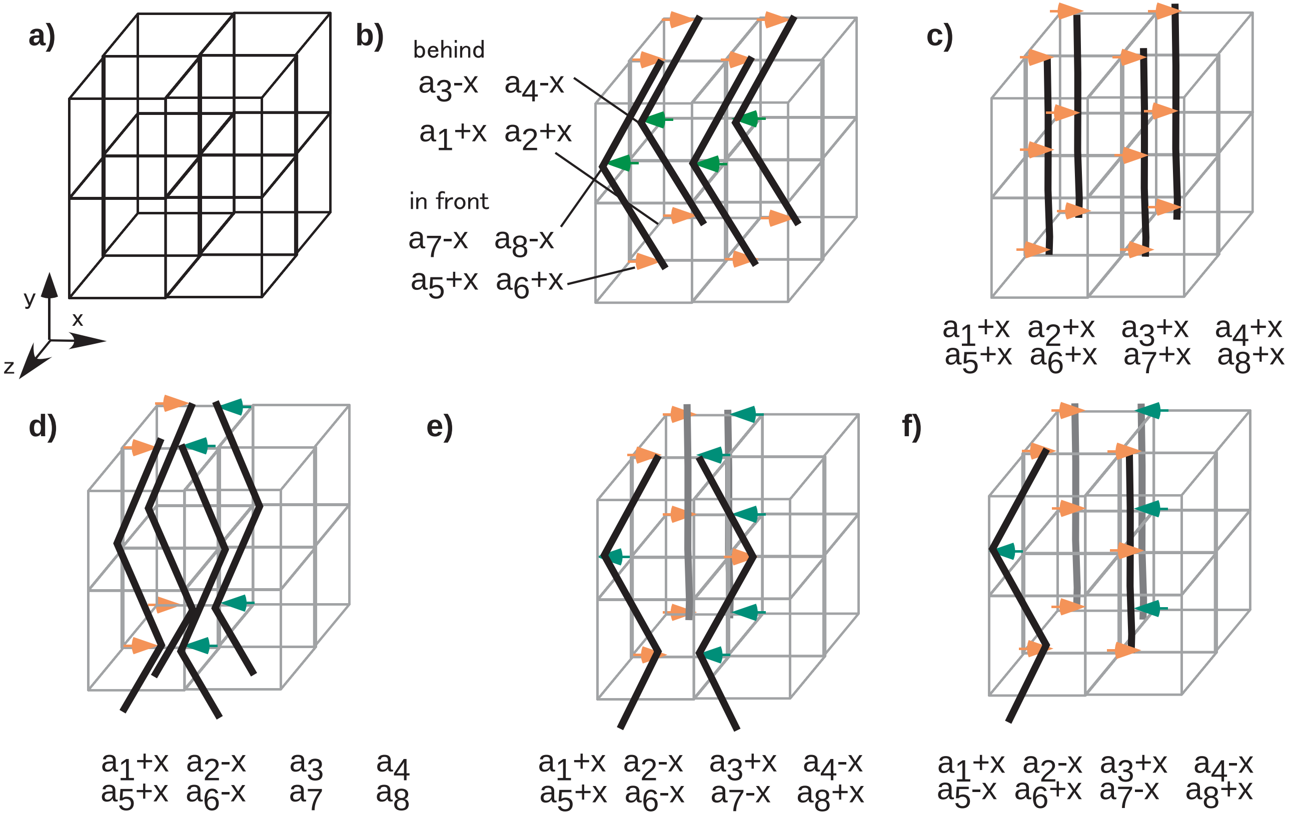
S-wave,
3-4km/s=
9000km/h





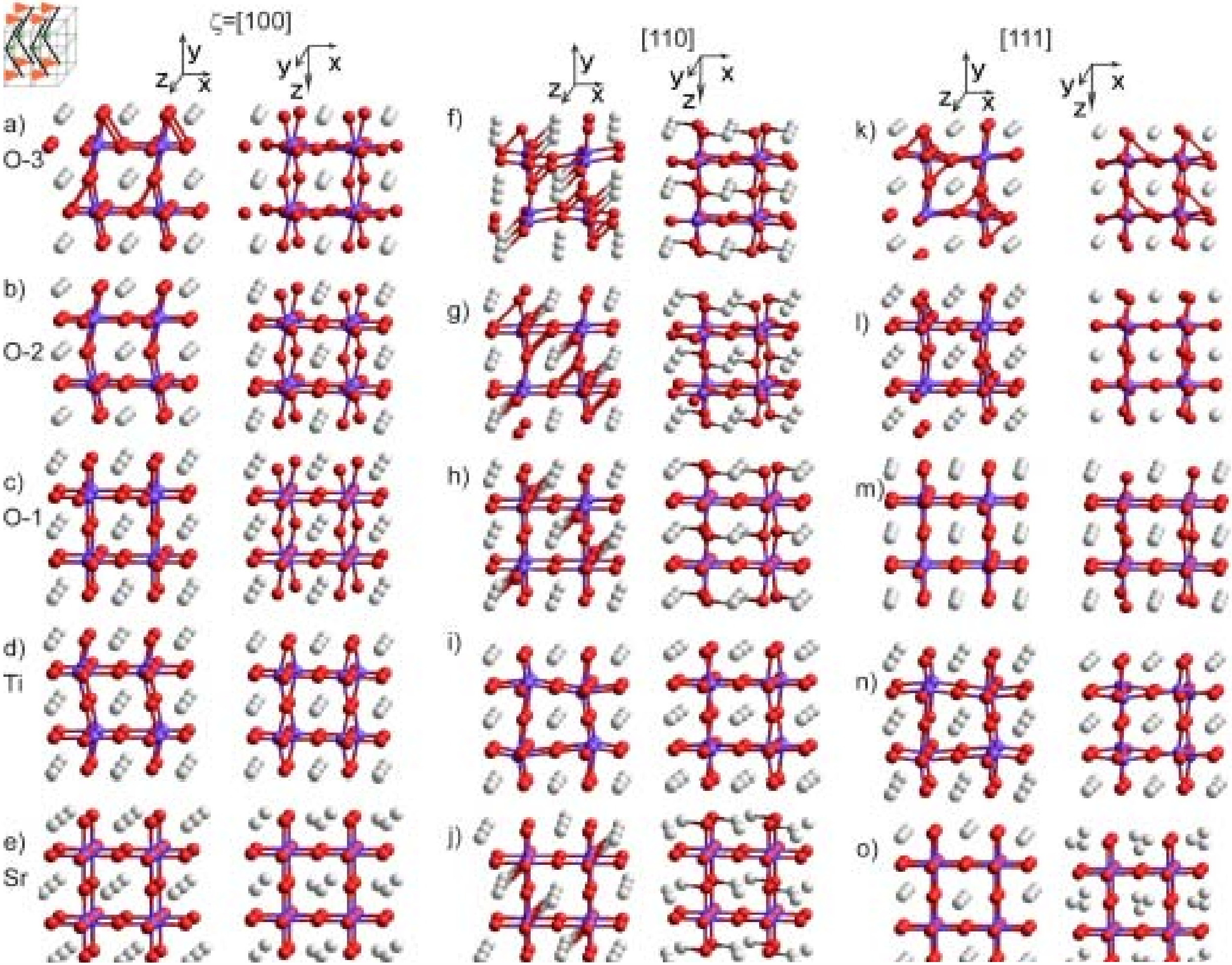


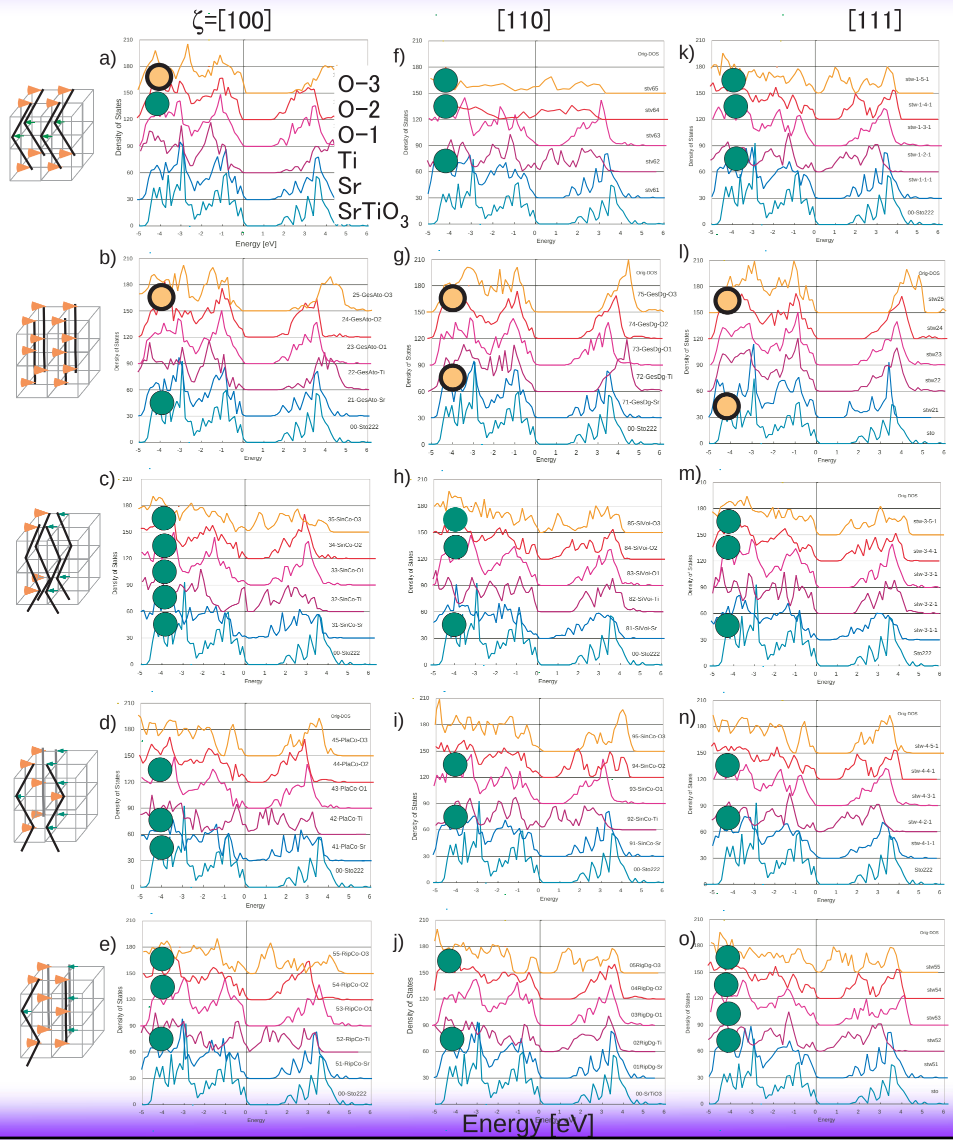
Frozen phonon calculations



Sr, Ti, 1O, 2O, 3O

Atomic structure of Frozen phonons





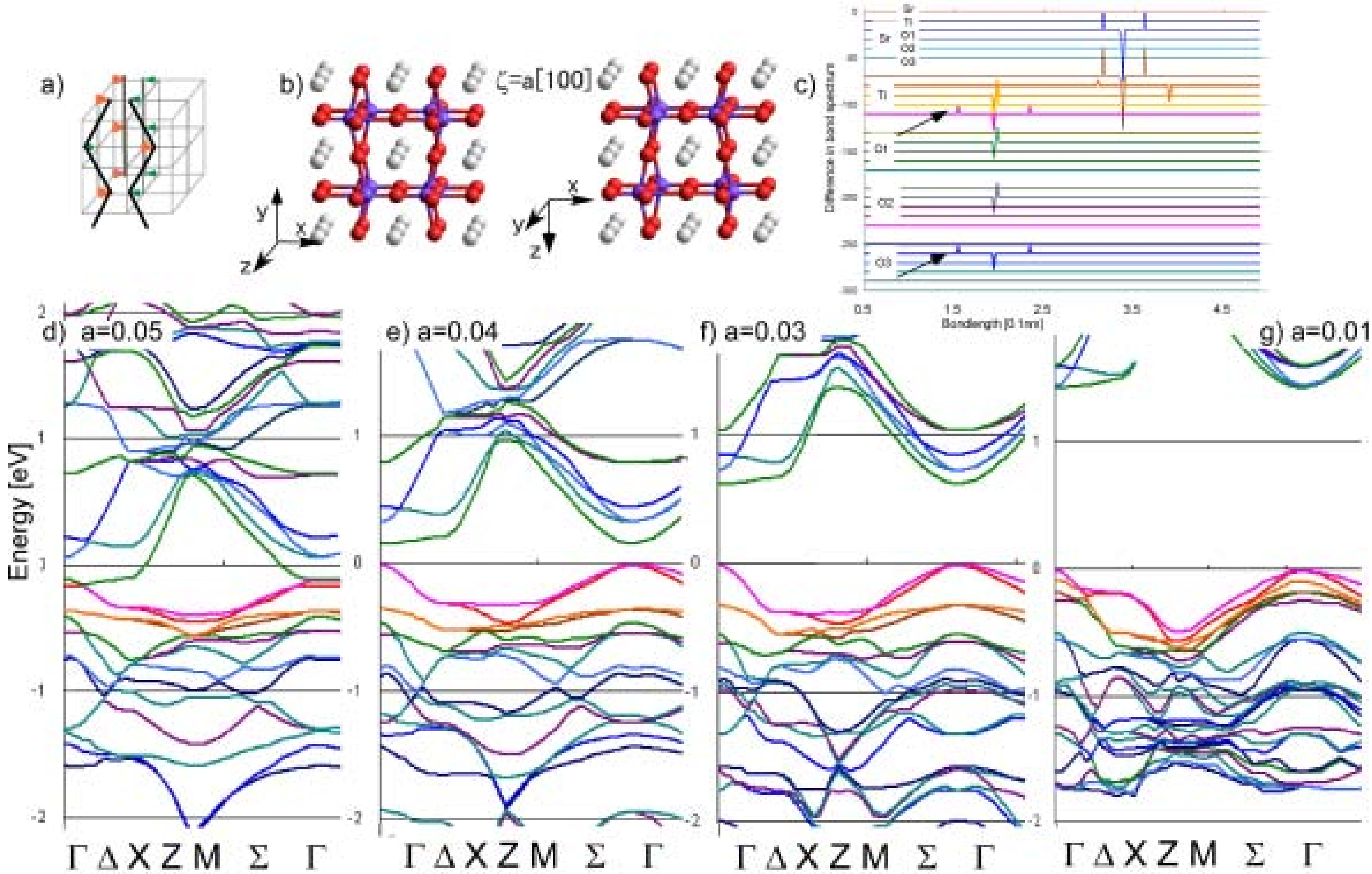
Electronic Band structure of frozen phonons

smaller bandgap

wider bandgap

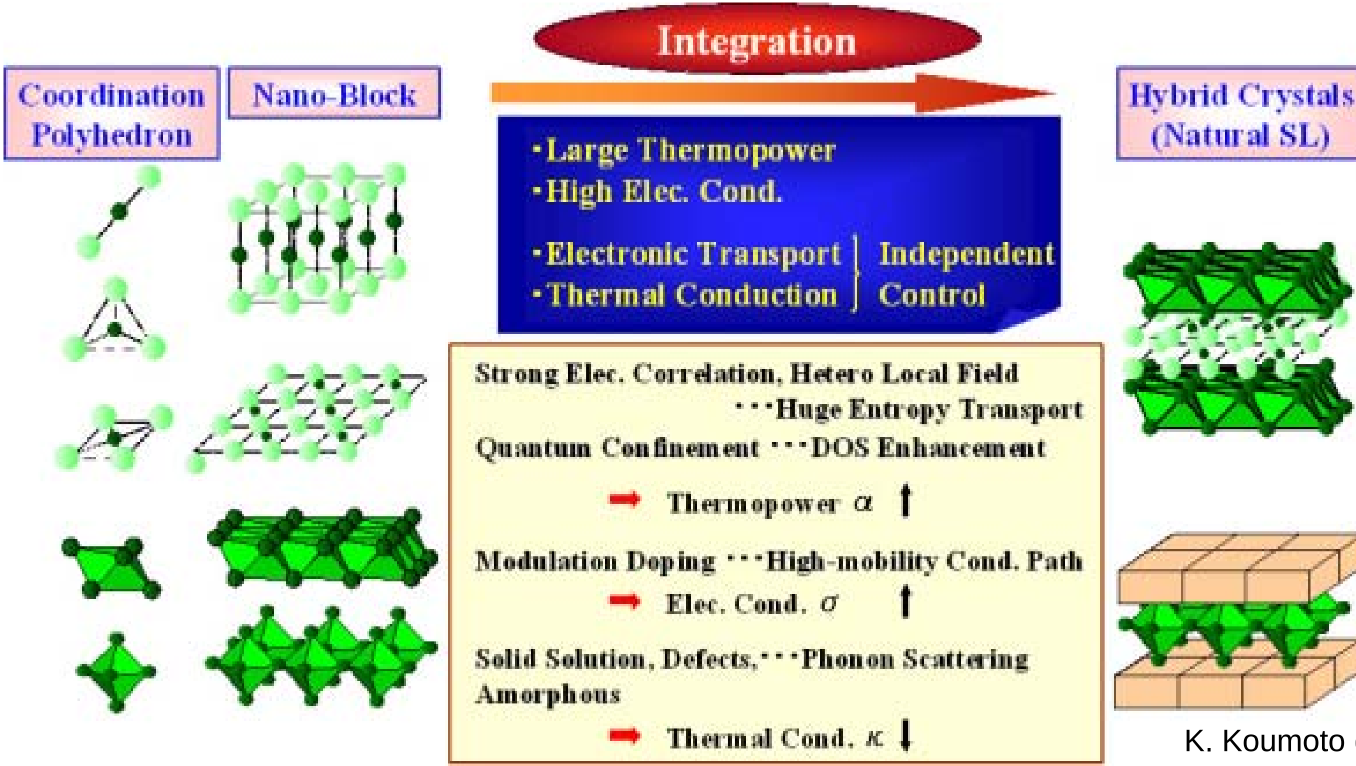
W.Wunderlich,
arxiv.org/abs/0711.0567

Electronic Bandstructure for a frozen phonon mode



-> Some phonon modes decrease the electronic bandgap

Nano-Doping -> Nano-Composite Material



K. Koumoto (2005)

5.Guideline: Search for proper interfaces

An atom is
the smallest unit for
doping an alloy.

→

An (coherent) Interface is
the smallest unit of
Nano-Composite Material.

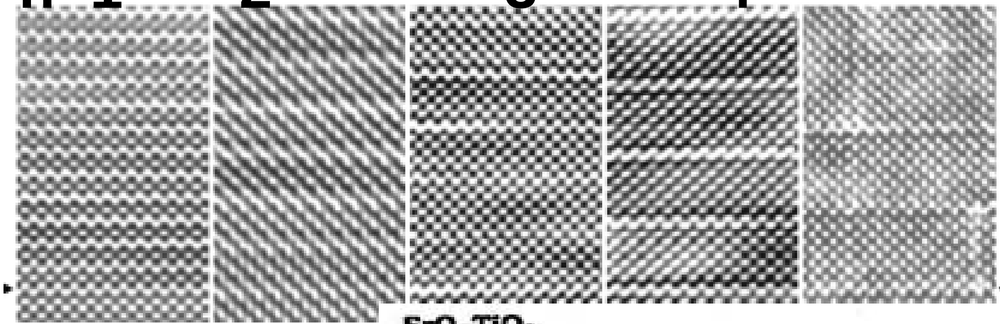
Ruddlesden-Popper "natural" Superlattice

Ruddlesden, S.N.;Popper, P. Acta Crys. 11 (1958) 54-55
J.H. Haeni, C.D.Theis, D.G. Schlom, et.al. APL 78 [21] (2001) 3292

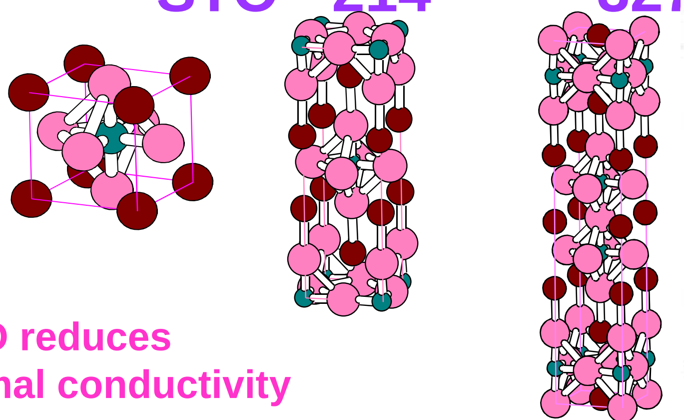
MBE-growth

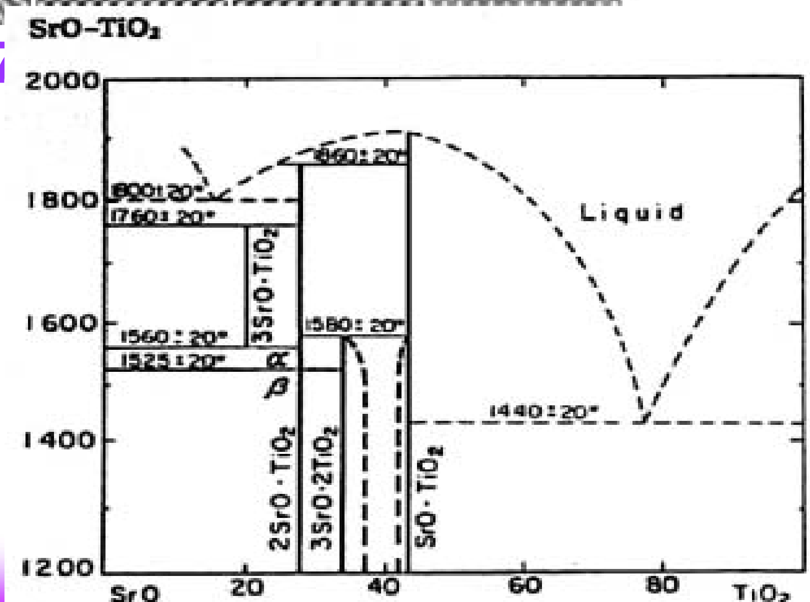
m=1 **n=1 2 3 4 5**

$(SrTiO_3)_n(SrO)_m$



STO- 214 327

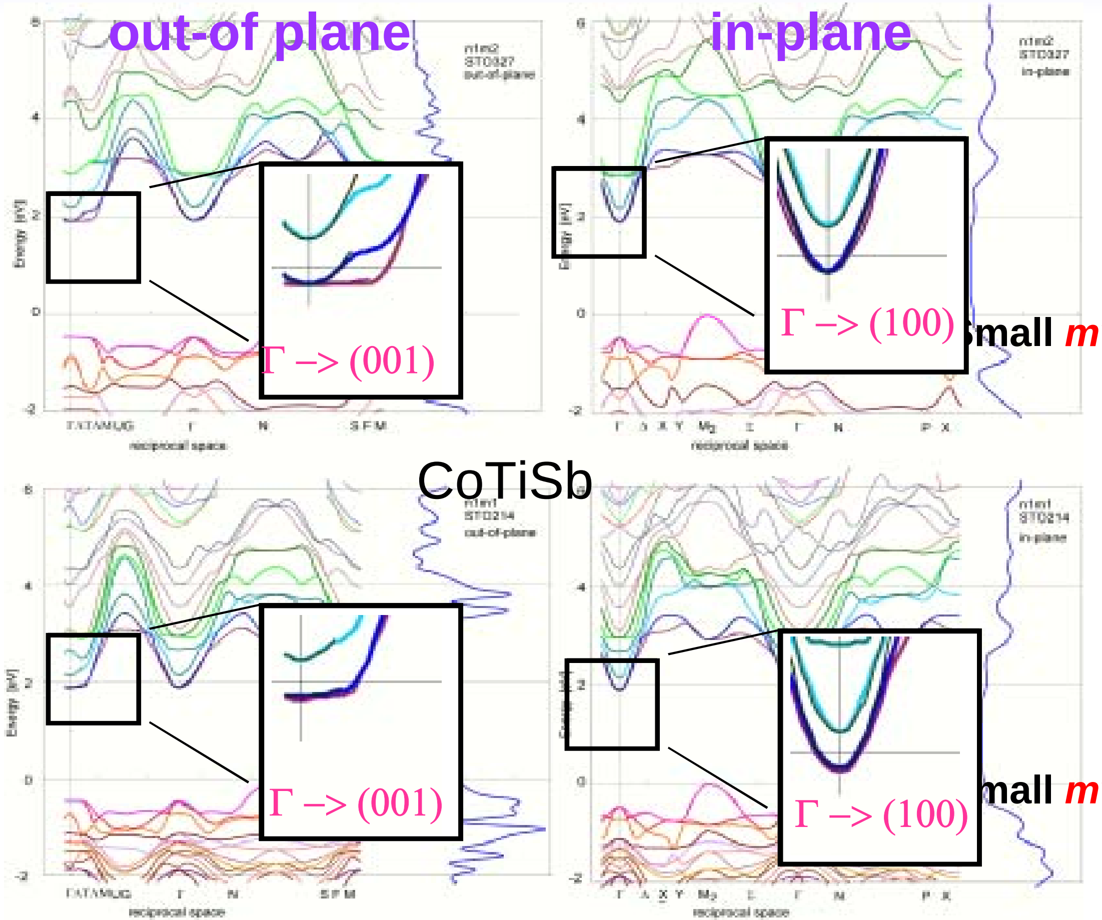




Idea: SrO reduces the thermal conductivity

Koumoto Proc.ICT 2004

Band structure of $SrTiO_3$-RP phases



STO327

Large *m*=10*

Small *m*=0.3*

STO214

Large *m*=6*

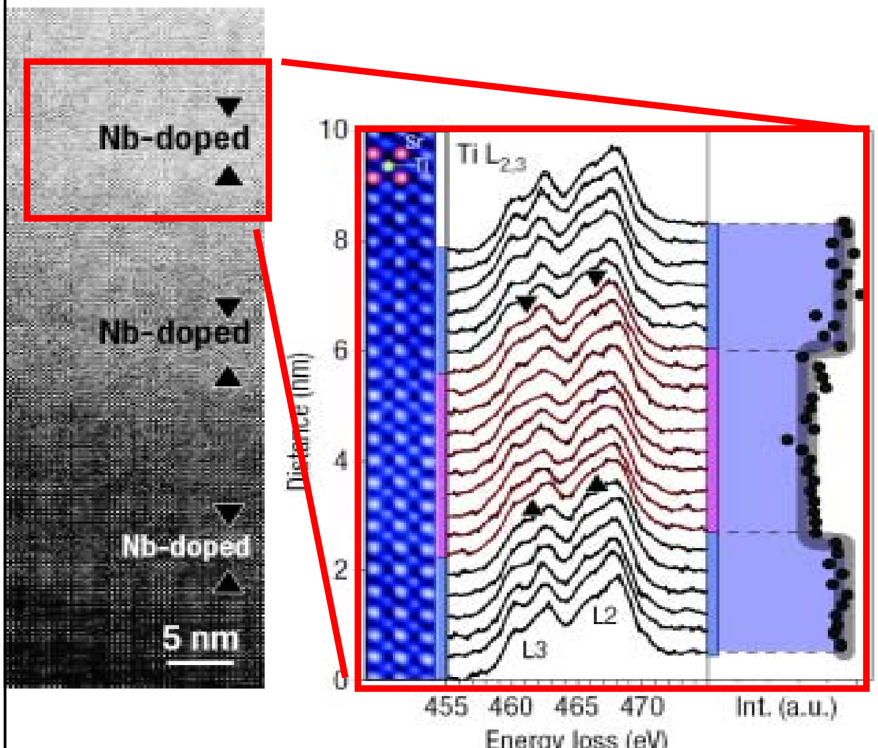
mall *m*=0.3*

->average 1.5

-> smaller effective mass than $SrTiO_3$

W.Wunderlich, K.Koumoto,et.al. Int.Conf.Thermoelectr. (2005) 237

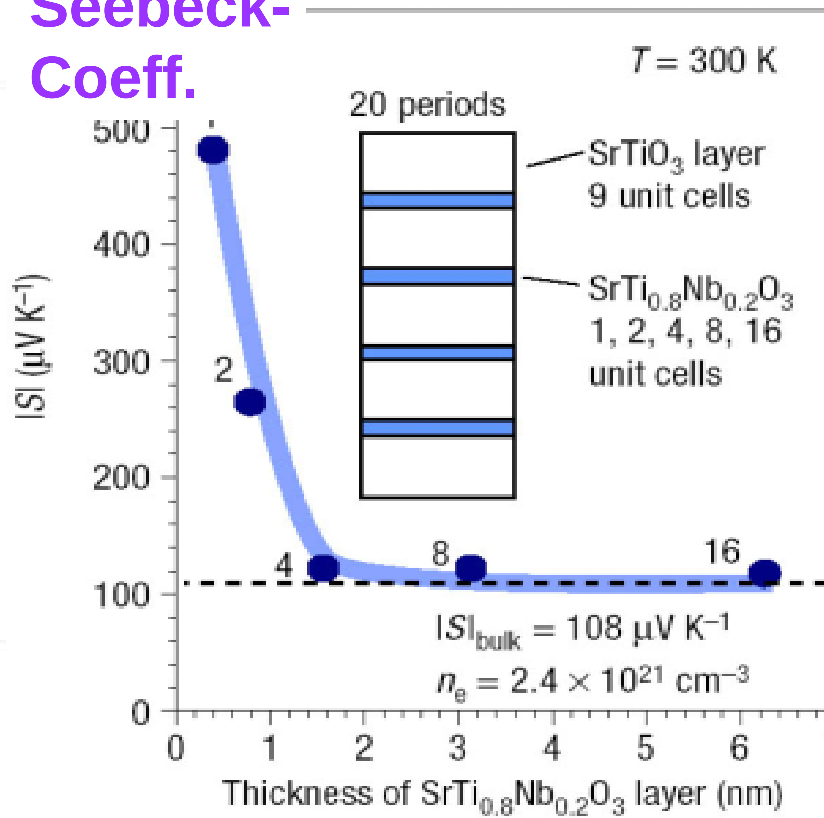
Giant Thermoelectric power of a 2DEG (1)



EELS in HAADF-STEM

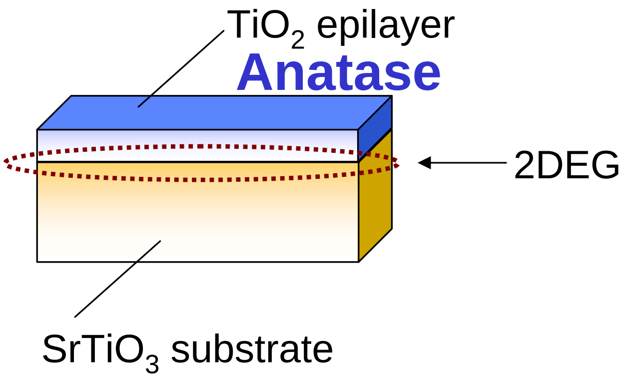
Ti^{4+} -> $Ti^{3+/4+}$

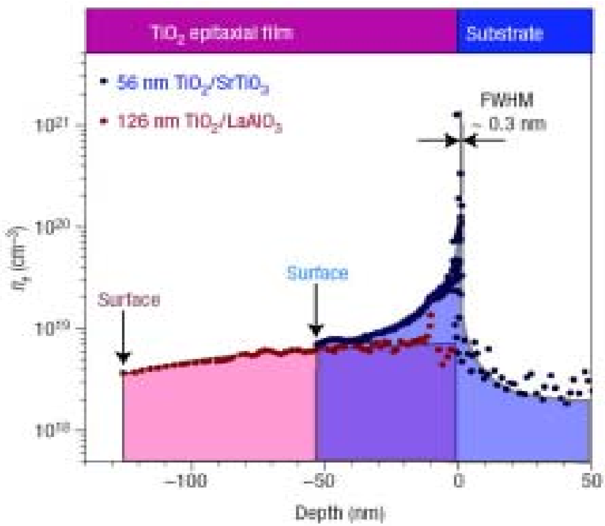
Seebeck-Coeff.

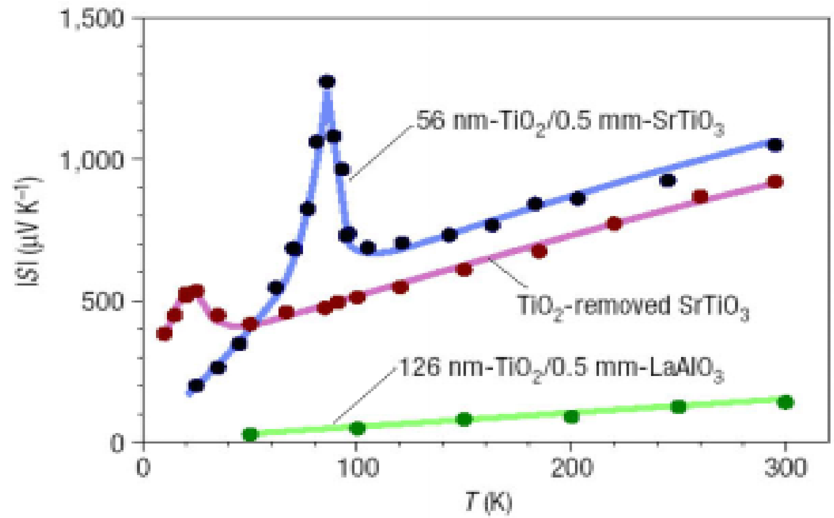


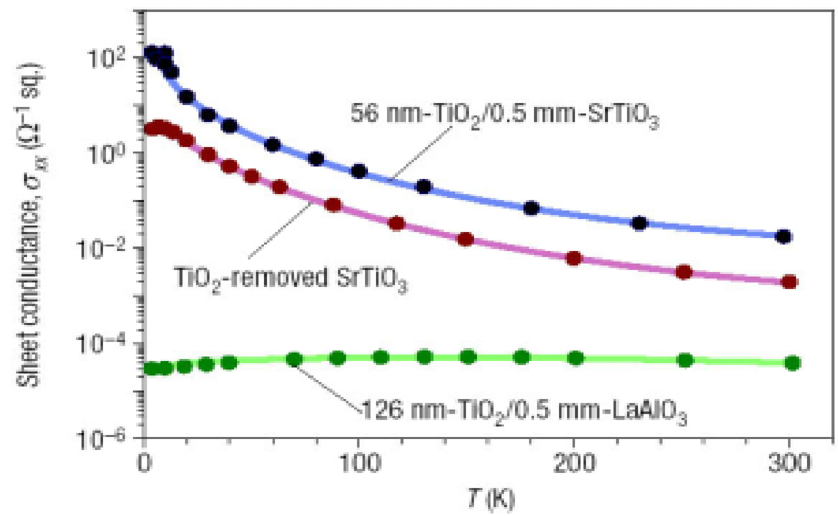
Ohta, K.,M.,M.,N.,O.,N.,N.,I.,H.,H.,Koumoto, Nature Materials 6 129 (2007)

Giant Thermoelectric power of a 2DEG









Ohta, Koumoto, et.al. Nature Materials 6 129 (2007)

Conclusion

- Nb-doped $SrTiO_3$ showed, that Large Effective mass is one of the parameters for large Seebeck-coefficient
- Certain Phonon modes decrease the bandgap due to shorther Ti-O bonds in $SrTiO_3$.
- Layered perovskites and $NaTaO_3$ are promising new TE-materials