Thermoelectric Oxide Materials For Electric Power Generation

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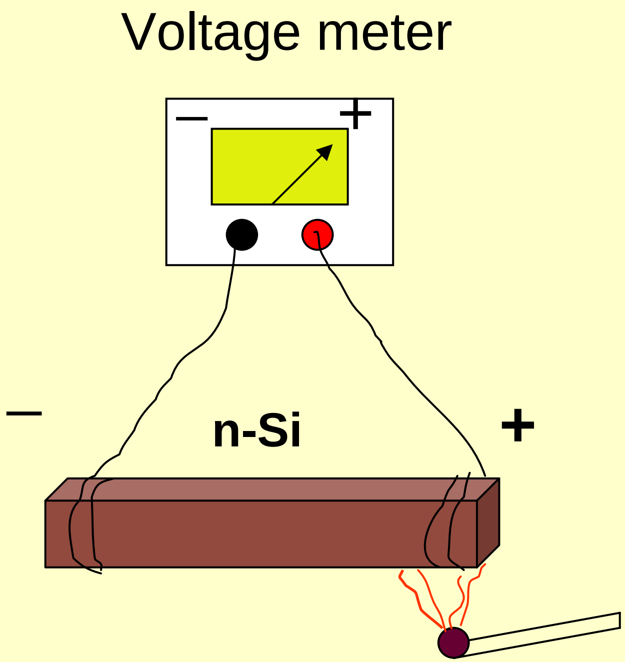
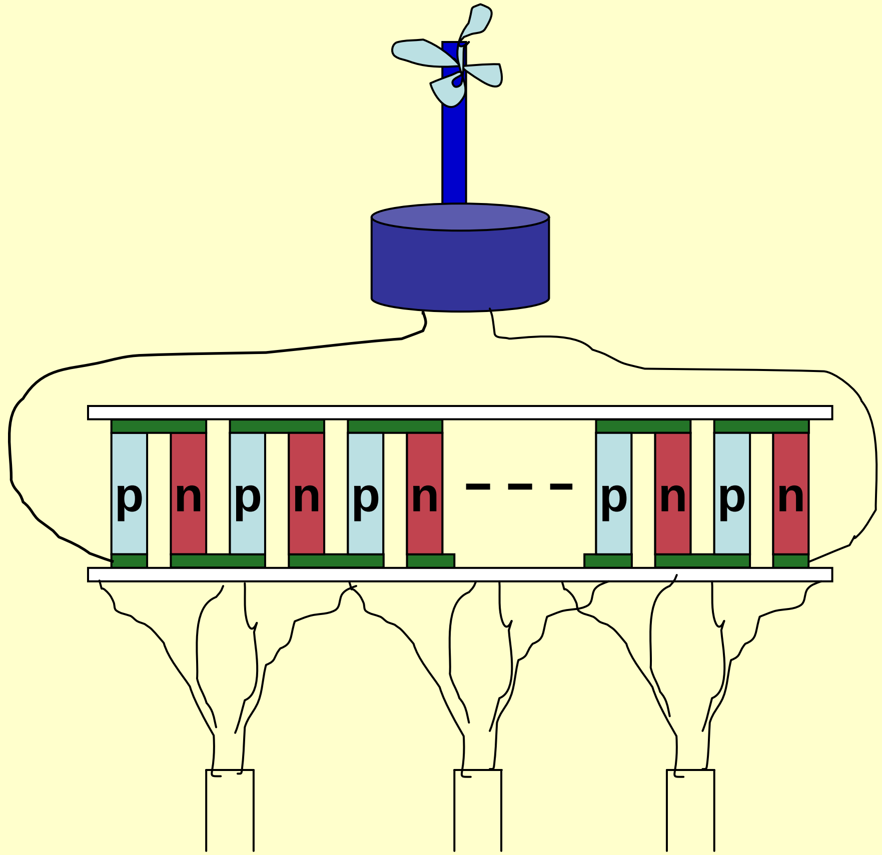
1. Thermoelectric Energy Conversion
2. Oxide Superlattices
3. Thin Film TE Devices

Seebeck Effect

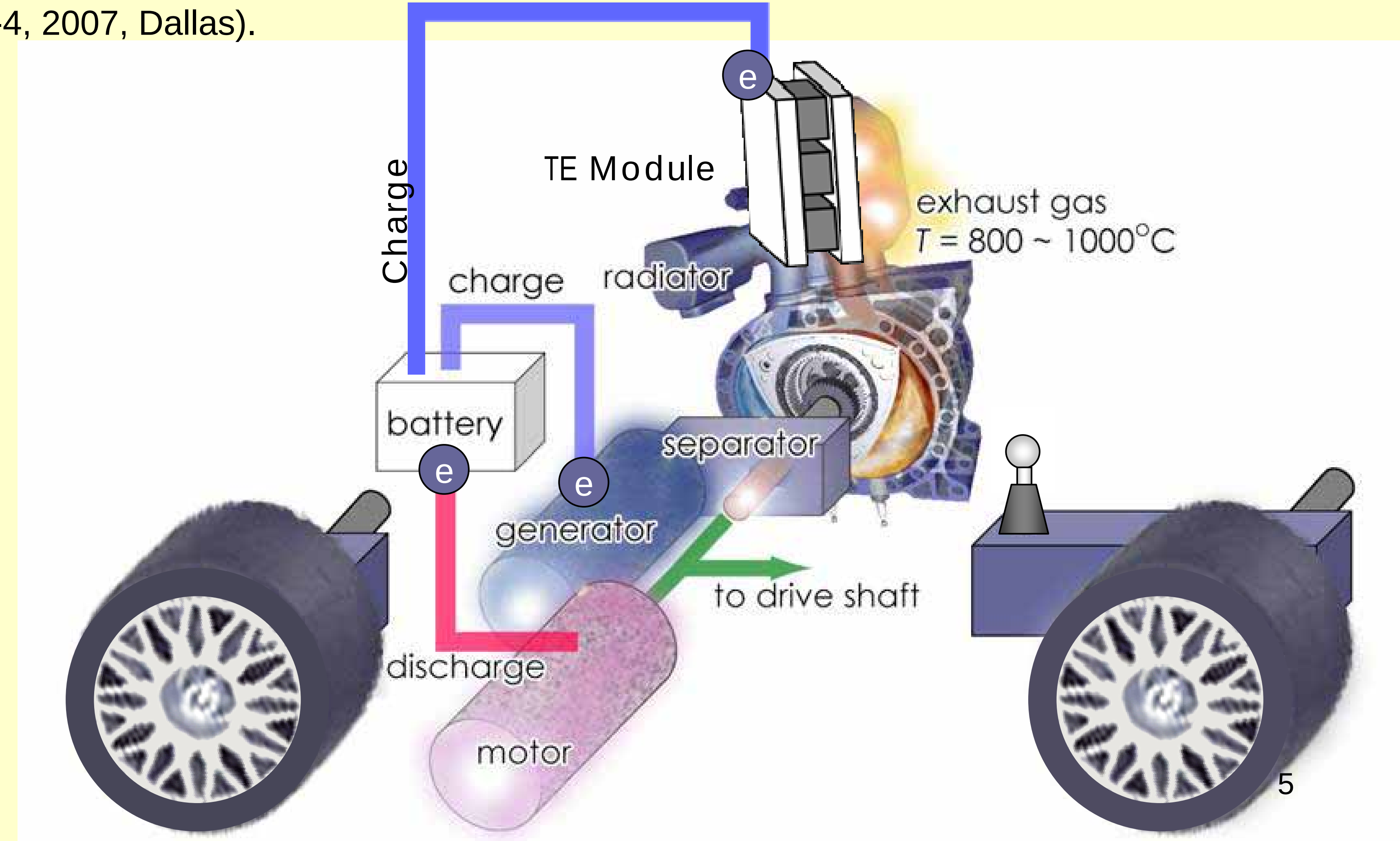


Power generation by a TE module



TE Technology for Waste Heat Recovery

"Even at the current efficiencies of thermoelectric devices, 7 to 8 percent, more than 1.5 billion gallons of diesel could be saved each year in the U.S. if thermoelectric generators were used on the exhaust of heavy trucks. That translates into billions of dollars saved." by Prof. T. Tritt (NanoTX'07 Conference,
Oct. 2-4, 2007, Dallas).



Problems of the Conventional TE Materials

Conventional materials: Bi_2Te_3, Sb_2Te_3, $PbTe$-Ag_2Te, $(Bi,Sb)_2Te_3$, $CoSb_3$, etc.

1. **Low Heat Resistance & Oxidation Resistance**

   Melting point of Bi_2Te_3 ： 580℃

   Comparison：Automobile exhaust gas 800 ~1000℃

2. **Limitation of resources**

   Very small Clarke Numbers

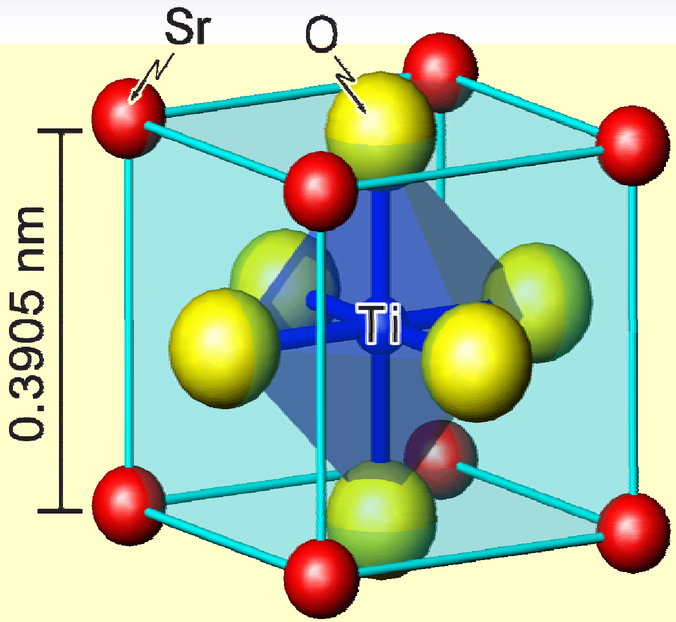
   Bi：2×10^{-5} %， Sb：5×10^{-5} %， Pb : 1.5×10^{-3} %， Te：2×10^{-7} %

   Ref. Pt : 5×10^{-7} %

3. **High toxicity**

Oxide TE Materials are highly wanted for power generation in air atmosphere !

$SrTiO_3$: Good Candidate

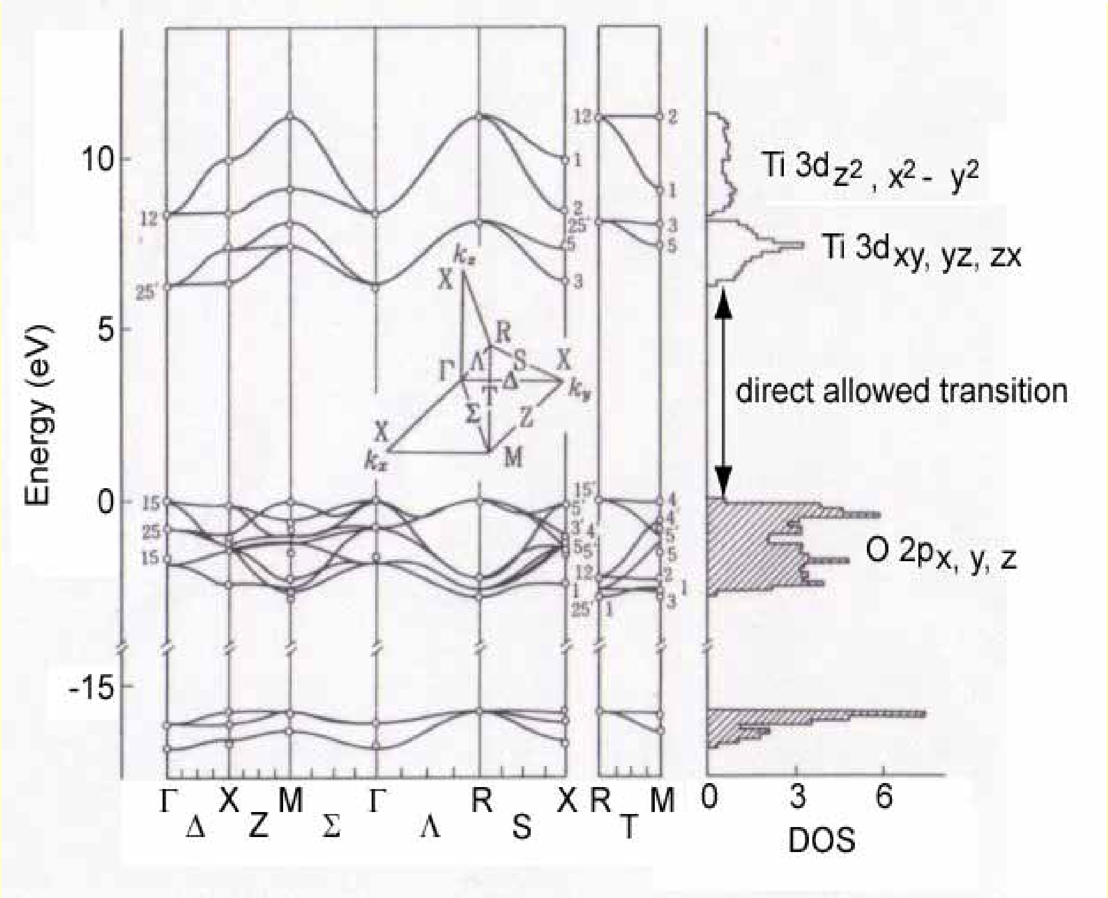


$SrTiO_3$ Single X'tal

E_g = 3.0~3.2 eV

m^*_{STO} = ~3-10m_0

(Frederikse *et al*. PR, 1964; Tokura *et al*. PRB, 2001)



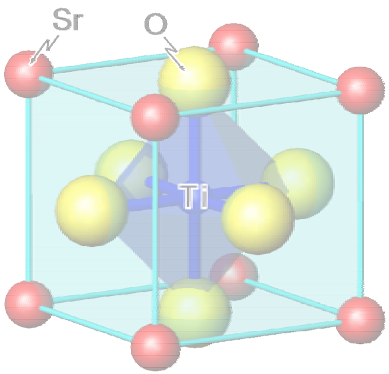
(L. F. Mattheiss,*et al* PRB., 1972)

Strategy

Cubic perovskite-type $SrTiO_3$

- Excellent controllability of electrical conductivity by doping
  - ➔ **High electrical conductivity, σ**
- Large carrier effective mass ($m^* = 6\text{-}11\ m_0$)
  - ➔ **Large Seebeck coefficient, $|S|$**
- The largest *ZT* among n-type TE oxides
  - ➔ **ZT = 0.37 @ 1000K ($SrTi_{0.8}Nb_{0.2}O_3$)**

[S. Ohta *et al*. *Appl. Phys. Lett.* **87** (2005)]



Improvement in *ZT* by reduction of thermal conductivity (κ)

and/or further enhancement of power factor (σS^2)

$$ZT = \sigma S^2 T / \kappa$$

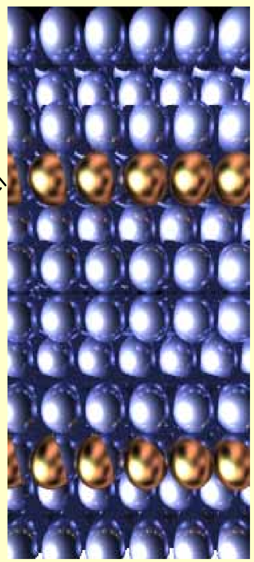
Superlattice

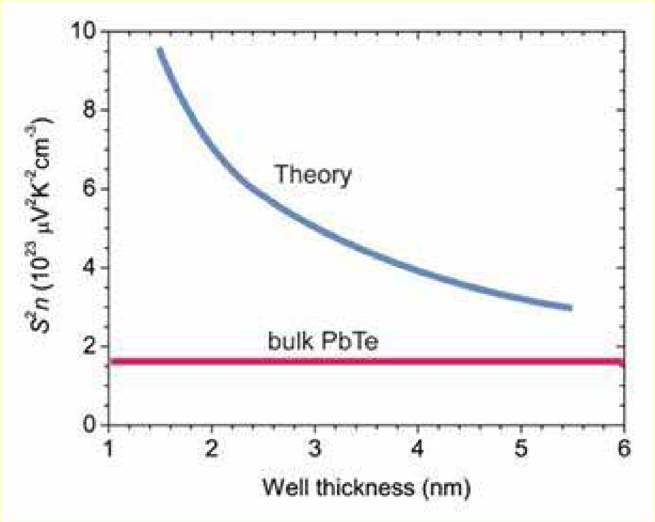
Artificial Superlattice

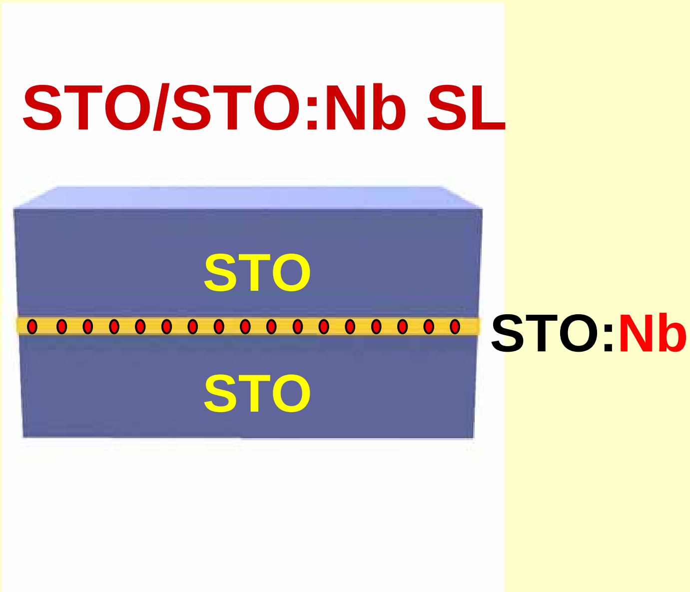
"If electrons were confined in a very narrow space, you would get enhanced thermopower!"

Hicks and Dresselhaus, Phys. Rev. *B* **47**, 12727 (1993).

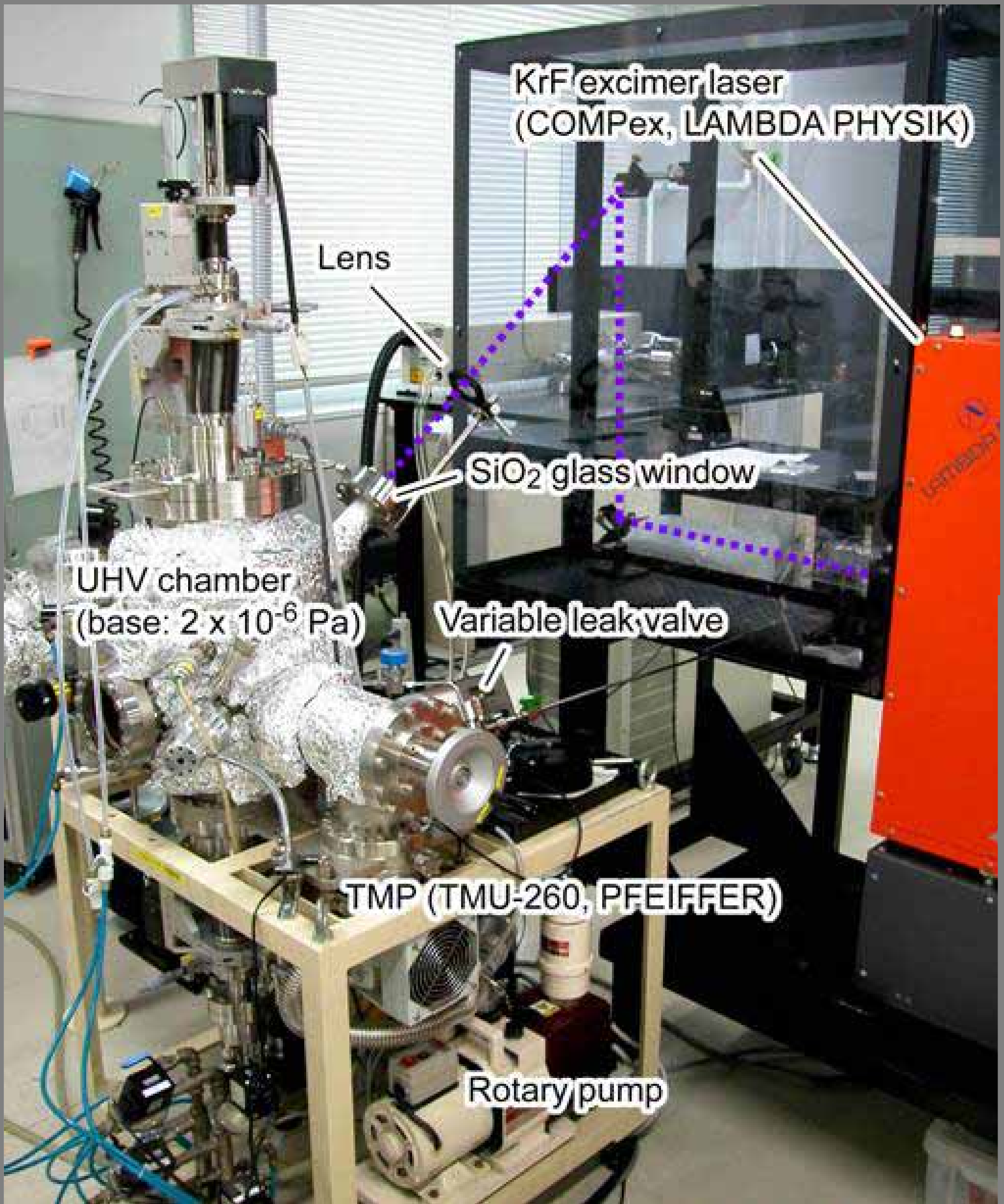
Thin layer with confined electrons

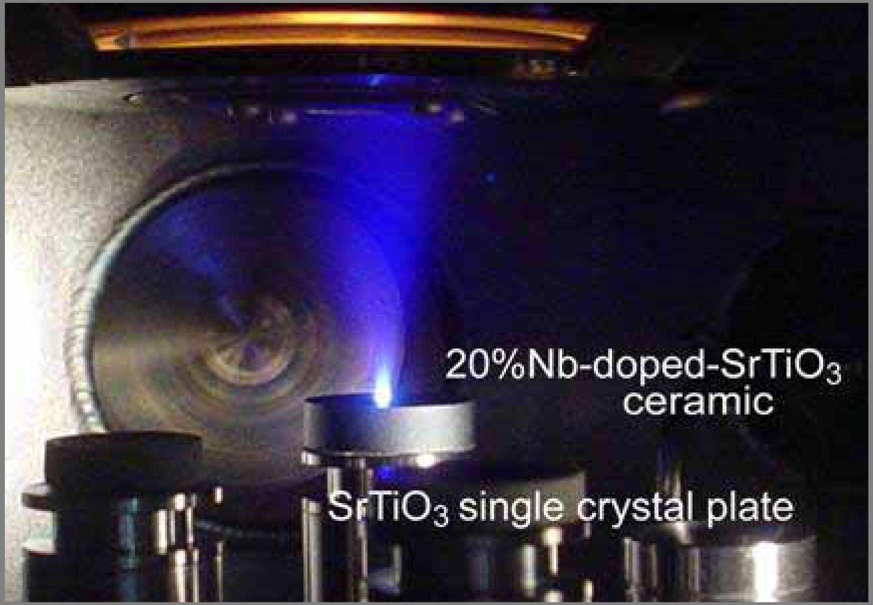






Fabrication of $SrTiO_3$/Nb:$SrTiO_3$ superlattice

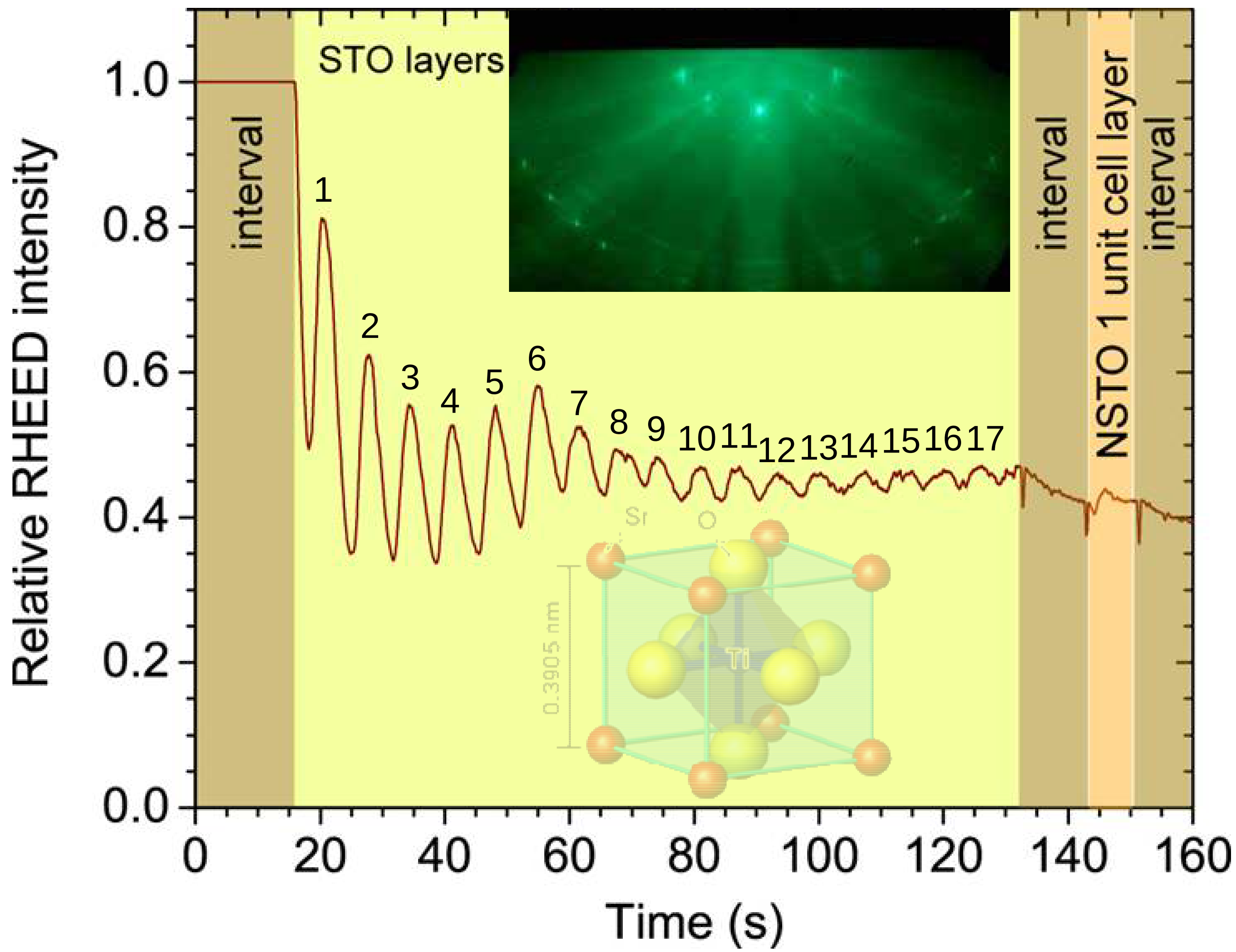




Growth condition

Substrate	(100)-$LaAlO_3$
Growth temp.	900°C
Oxygen pressure	3 x 10^{-3} Pa
Laser energy density	~1 $Jcm^{-2}pulse^{-1}$
Repetition rate	10 Hz
Growth rate	~50 pm s^{-1}

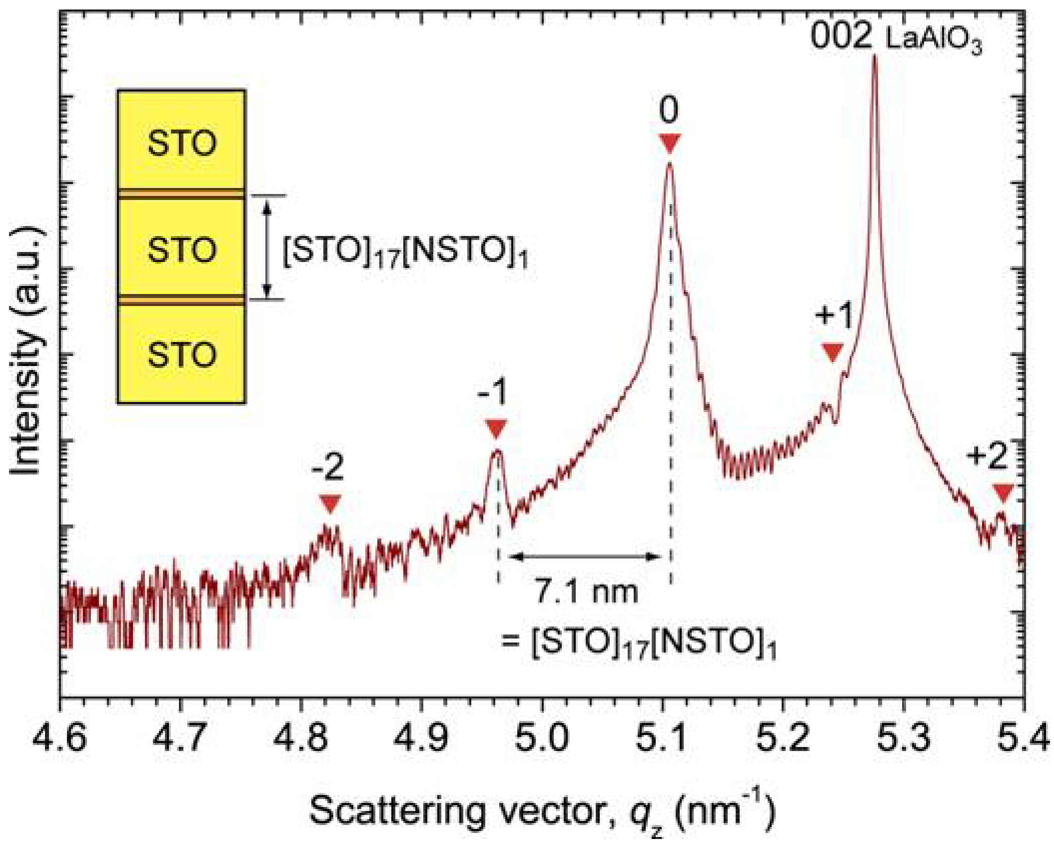
RHEED intensity oscillation



XRD & AFM

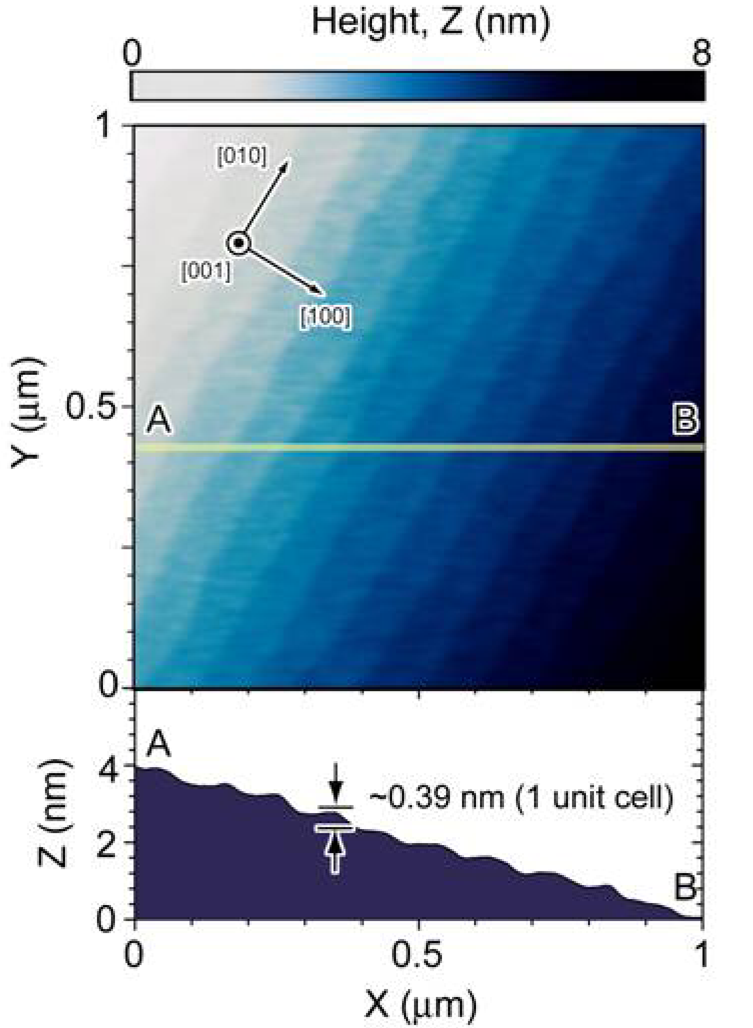
Out-of-plane XRD pattern

Satellite peaks due to superlattice are clearly seen

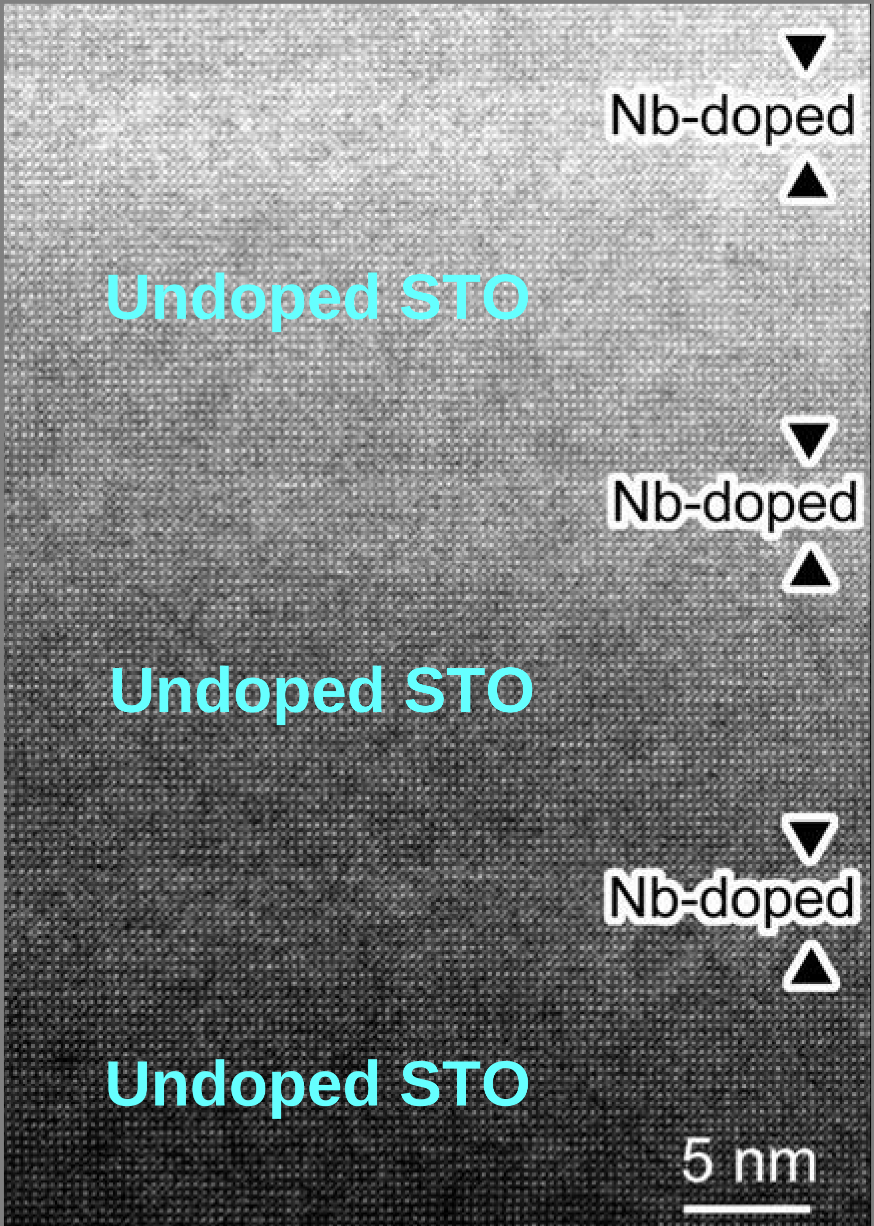


Topographic AFM image

Frank Van der Merwe (2D) growth

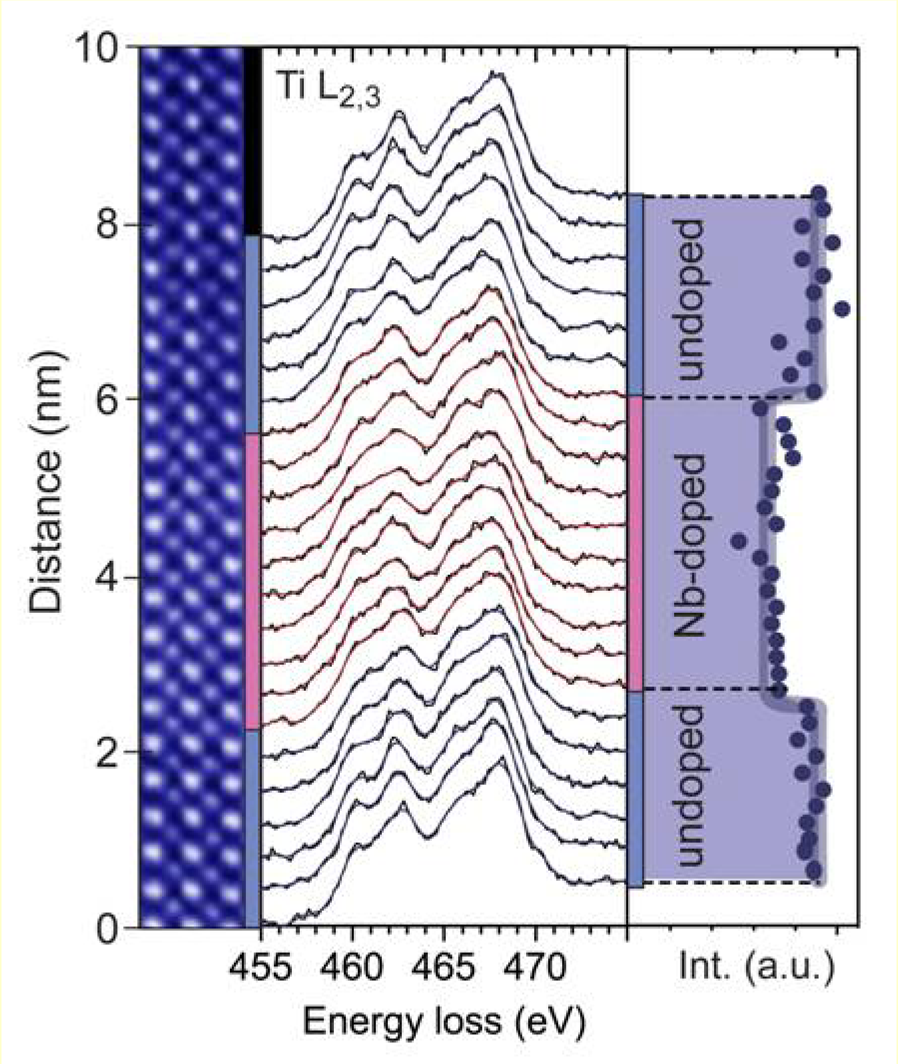


HAADEF-STEM & HREELS

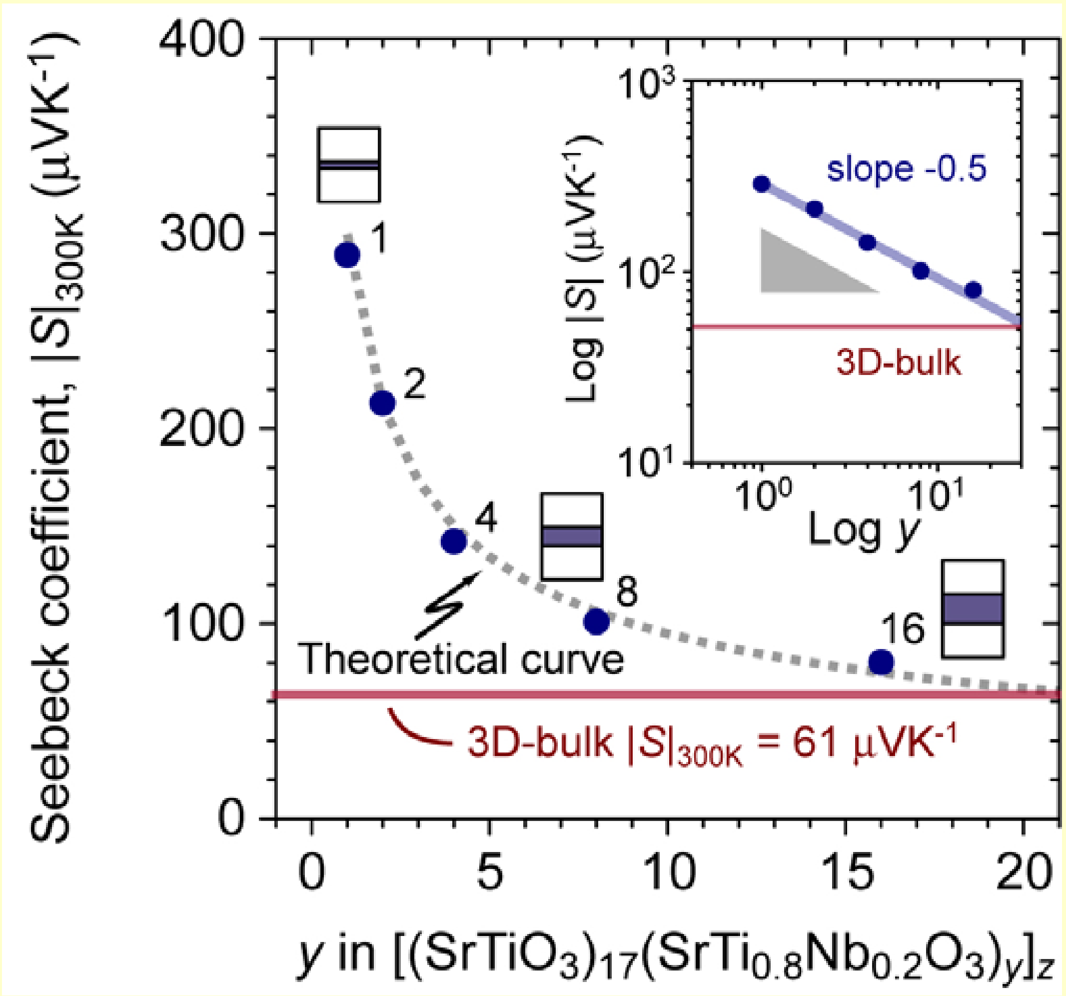


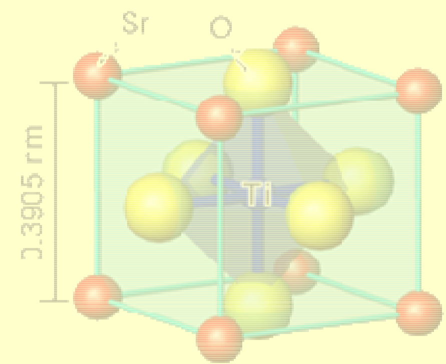
HREELS

Diffusion of dopant Nb did not take place!



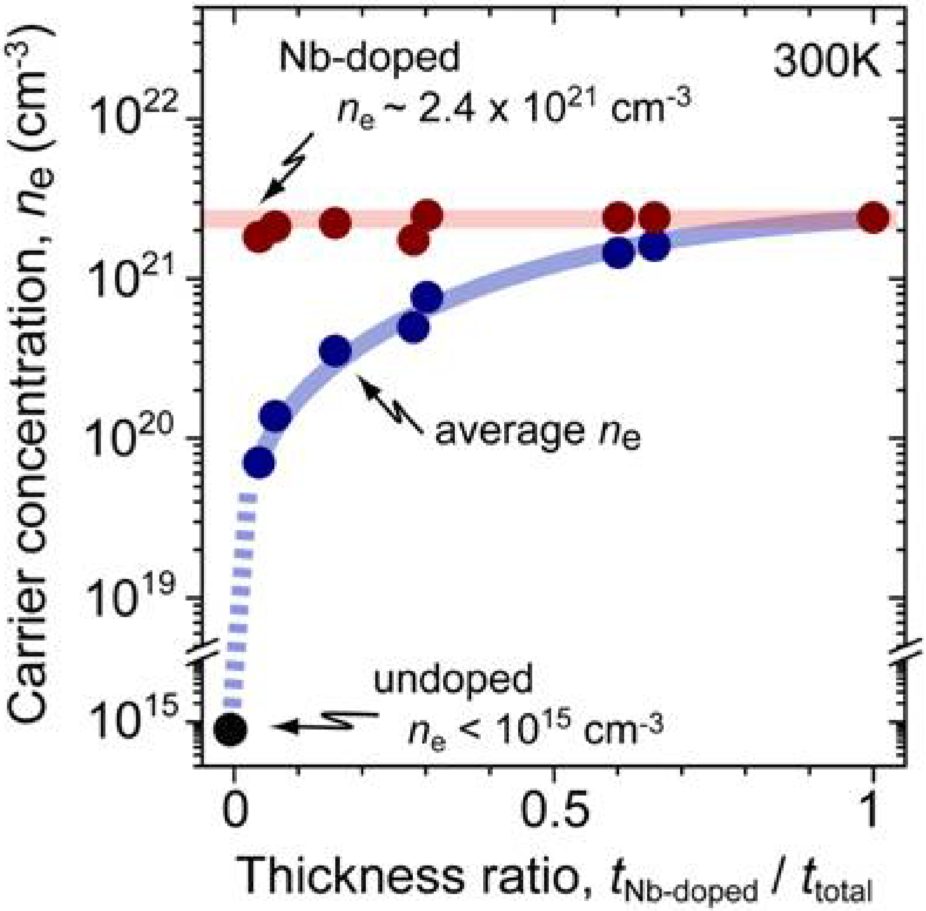
Seebeck coefficient vs. well thickness





H. Ohta et al.,
***Nature Mater.*, 6, 129 (2007)**

Electrical Conductivity



Nb-doped STO Layer

Electrical conductivity

σ = 2.3 x 10^3 Scm^{-1} at 300K

Hall mobility

μ_{Hall} ~ 6 cm^{2}V^{-1}s^{-1} at 300K

Carrier concentration

n_e = 2.4 x 10^{21} cm^{-3} at 300K

H. Ohta et al.,
Nature Mater., **6**, 129 (2007)

Thermoelectric figure of merit, *ZT*

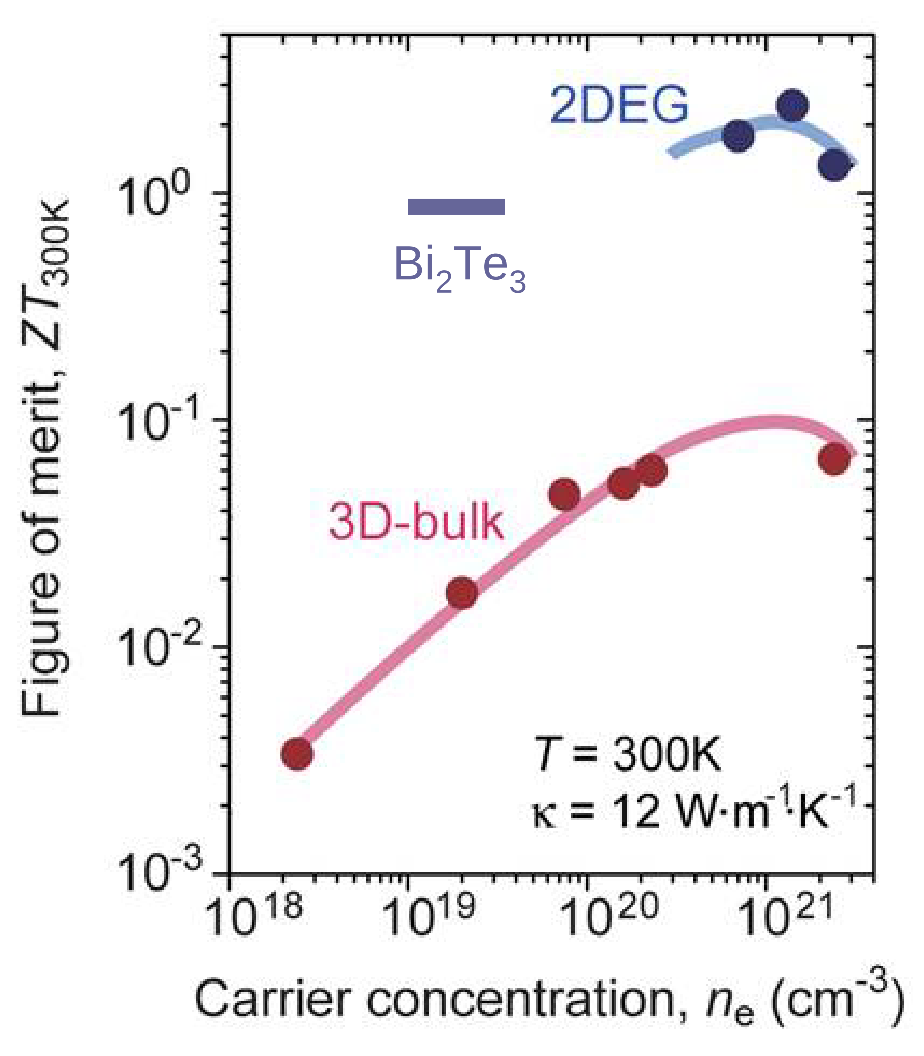


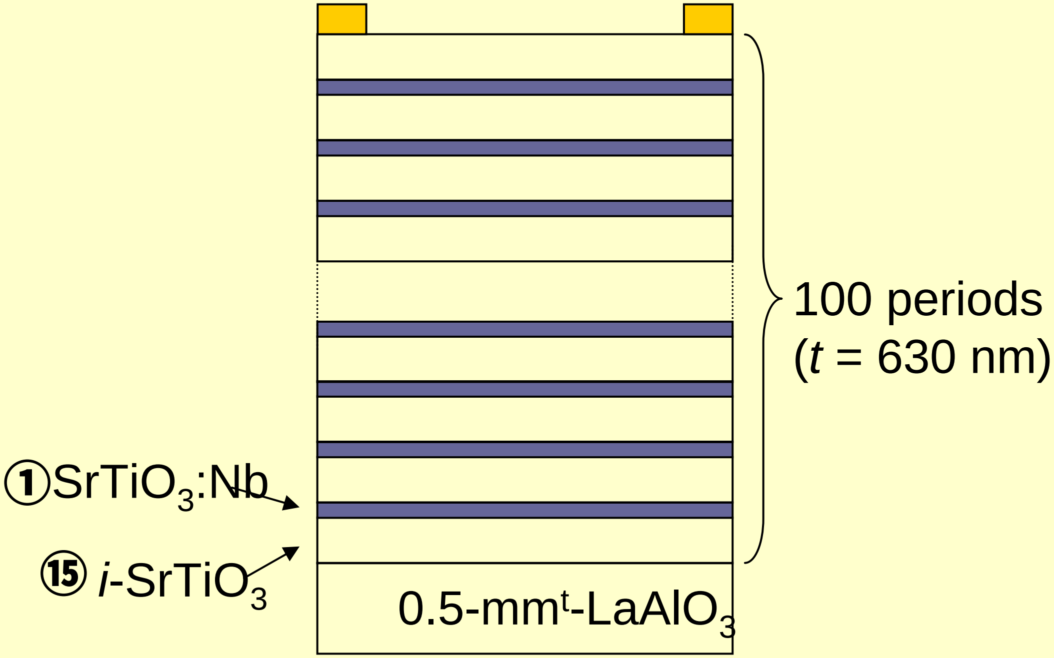
Figure of merit *ZT*

The optimized ZT value in the 2DEG system reaches ZT_{300K}(2DEG)= 2.4, which is 24 times larger than that of the corresponding 3D-bulk $SrTiO_3$

Cf: **Bi_2Te_3/Sb_2Te_3 SL**
ZT_{300K}= 2.4
(Venkatasubramanian et al., *Nature*, 2001)

H. Ohta et al.,
Nature Mater., **6**, 129 (2007)

Direct Heating Test : STO/STO:Nb Superlattice



50 mV@ ΔT=140 K

1 unit cell SrTiO$_3$:Nb

Carrier electron concentration, $n_e = 4\times10^{21}$ cm^{-3}

Hall mobility, $\mu_{Hall300K}$ = 5 cm$^2\cdot$V$^{-1}\cdot$s^{-1}

Electrical conductivity, σ_{300K} = 3,200 S$\cdot$cm^{-1}

Seebeck coefficient, $|S|_{300K}$ = 350 μV$\cdot$K^{-1}

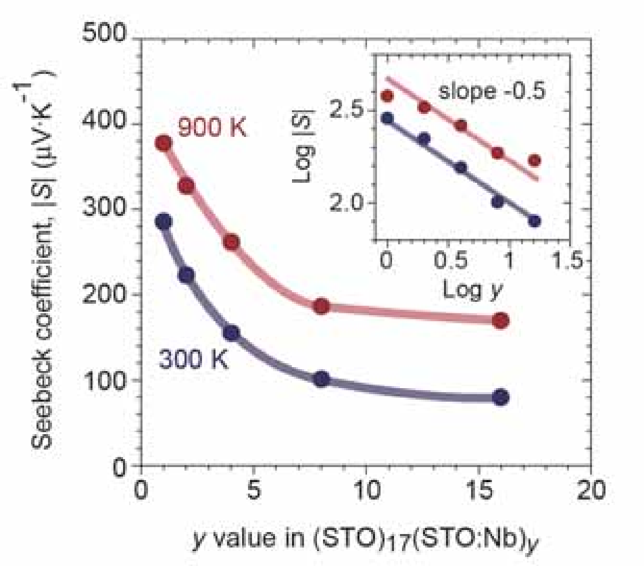
Cf: **Bi_2Te_3**

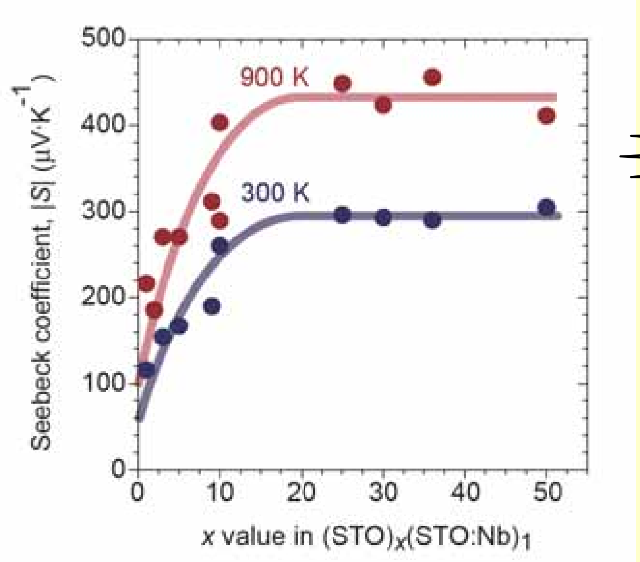
σ_{300K} = 1,200 Scm^{-1}

S_{300K} = 200 μV K^{-1}

28 mV @ ΔT=140 K

High-Temp. Characteristics of STO/STO:Nb SL





TE Conversion Efficiency of Superlattice

T_c = 300 K , T_h = 900 K
ZT = 2.4 @ 300 K, ZT = 1.4 @ 900 K
ZT(average) ∼ 1.9 is assumed.

$$\eta = \frac{W_{out}}{Q_{in}} = \frac{T_h - T_c}{T_h} \frac{(1+ZT_m)^{1/2} - 1}{(1+ZT_m)^{1/2} + \frac{T_c}{T_h}}$$

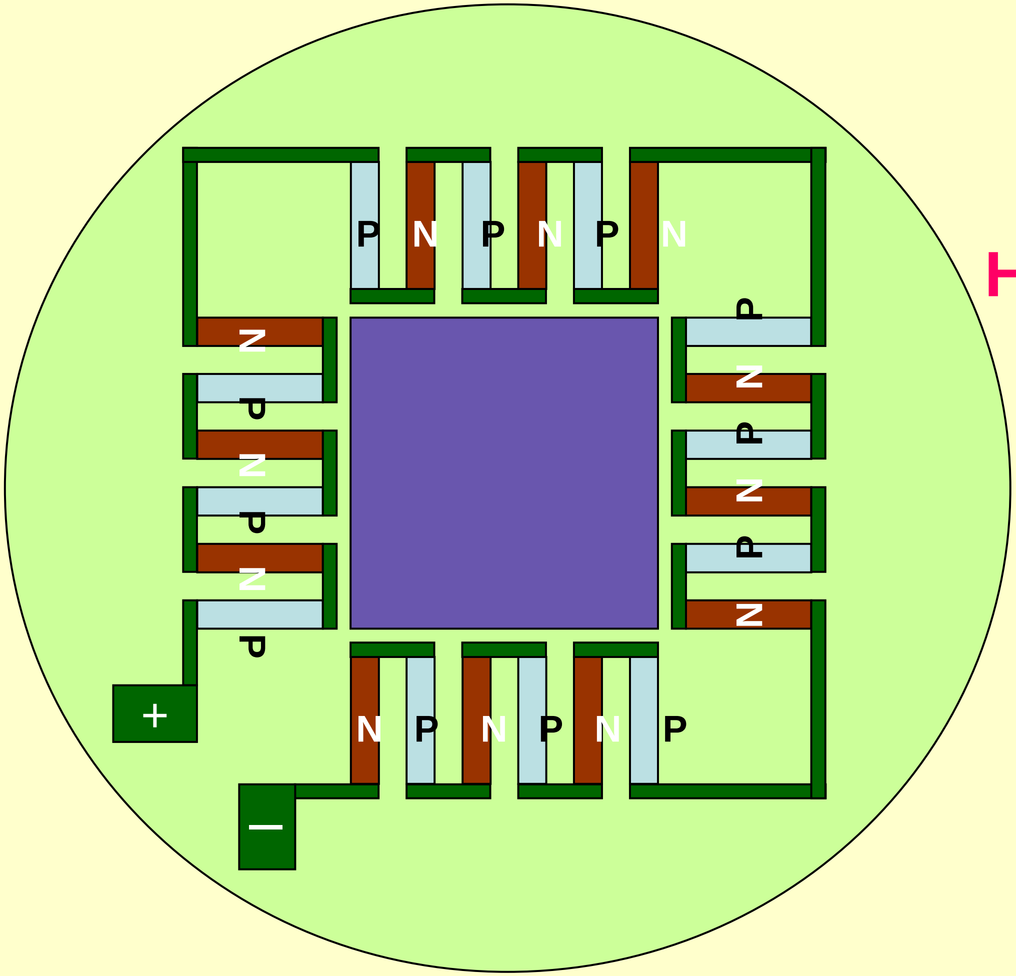
TE.C.E η ∼ 22%

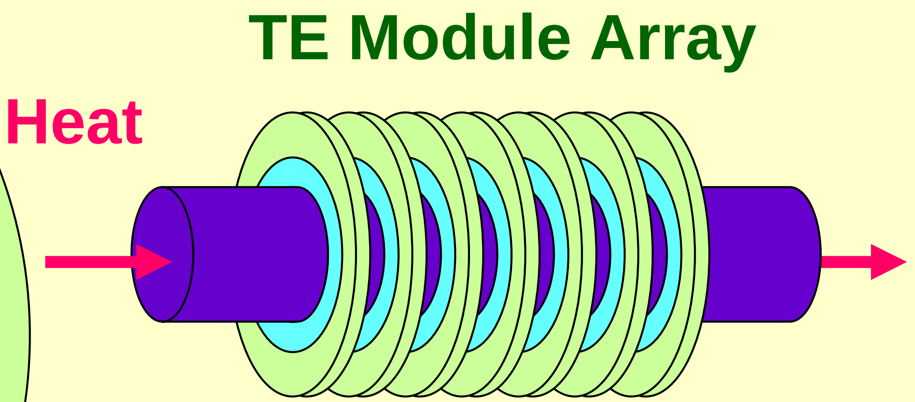
Cf: **Bi_2Te_3** T_c=300 K , T_h=500 K
ZT(average) ~ 1.0 η∼8.2%

Design Concept for TE Thin Film Module

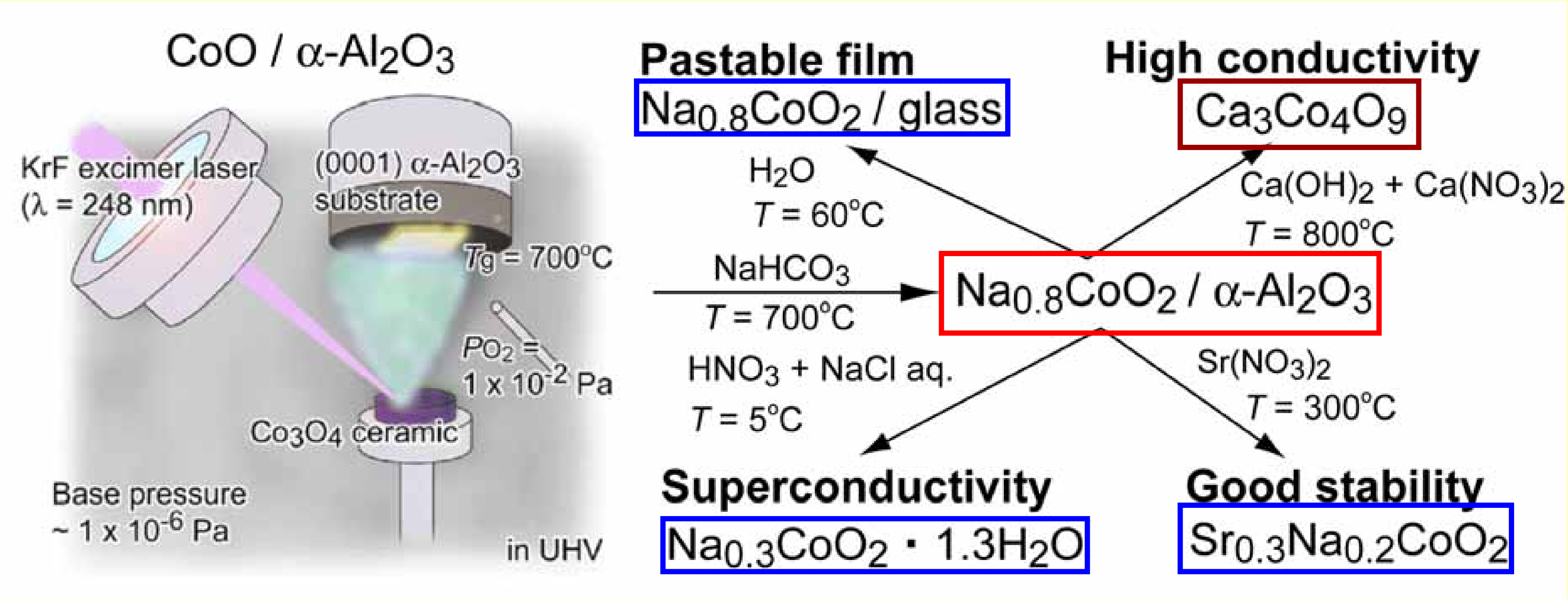
N-type TE element : STO/STO:Nb Superlattices

P-type TE element : $Ca_3Co_4O_9$ Thin Films





P-type Layered Cobalt Oxide for TE Thin Film Module



H. Ohta et al., *Cryst. Growth & Design*, **5**, 215-218 (2005).
K. Sugiura et al., *Appl. Phys. Lett.*, **88**, 082109 (2006).
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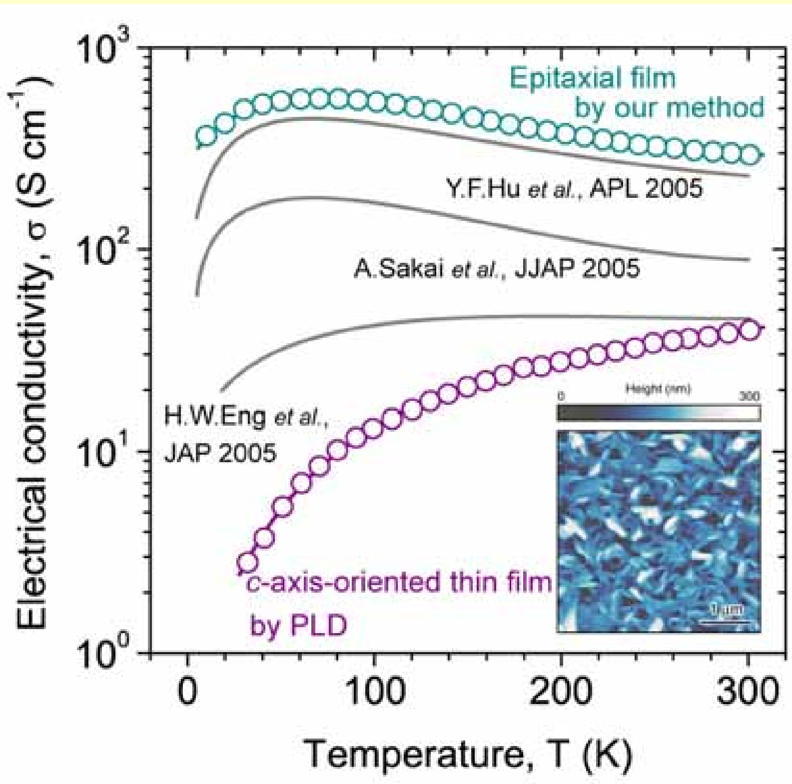
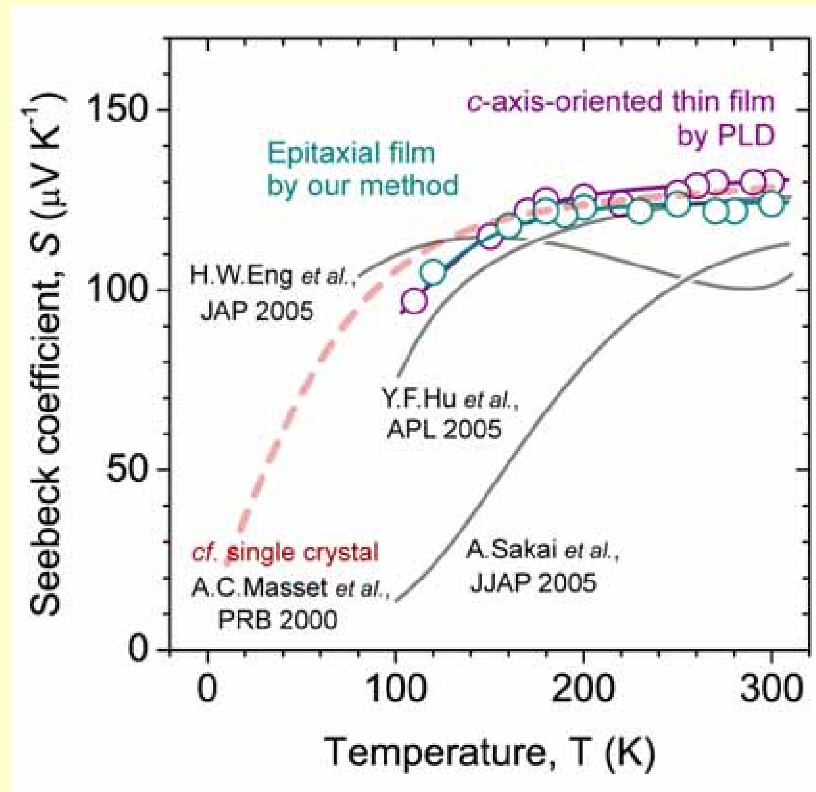
K. Sugiura et al., *Appl. Phys. Lett.*, **89**, 032111 (2006).
H. Ohta et al., *Adv. Mater.*, **18**, 1649-1452 (2006).
K. Sugiura et al., *Int. J. Adv. Ceram. Technol.*, **4**, 308-317 (2007).

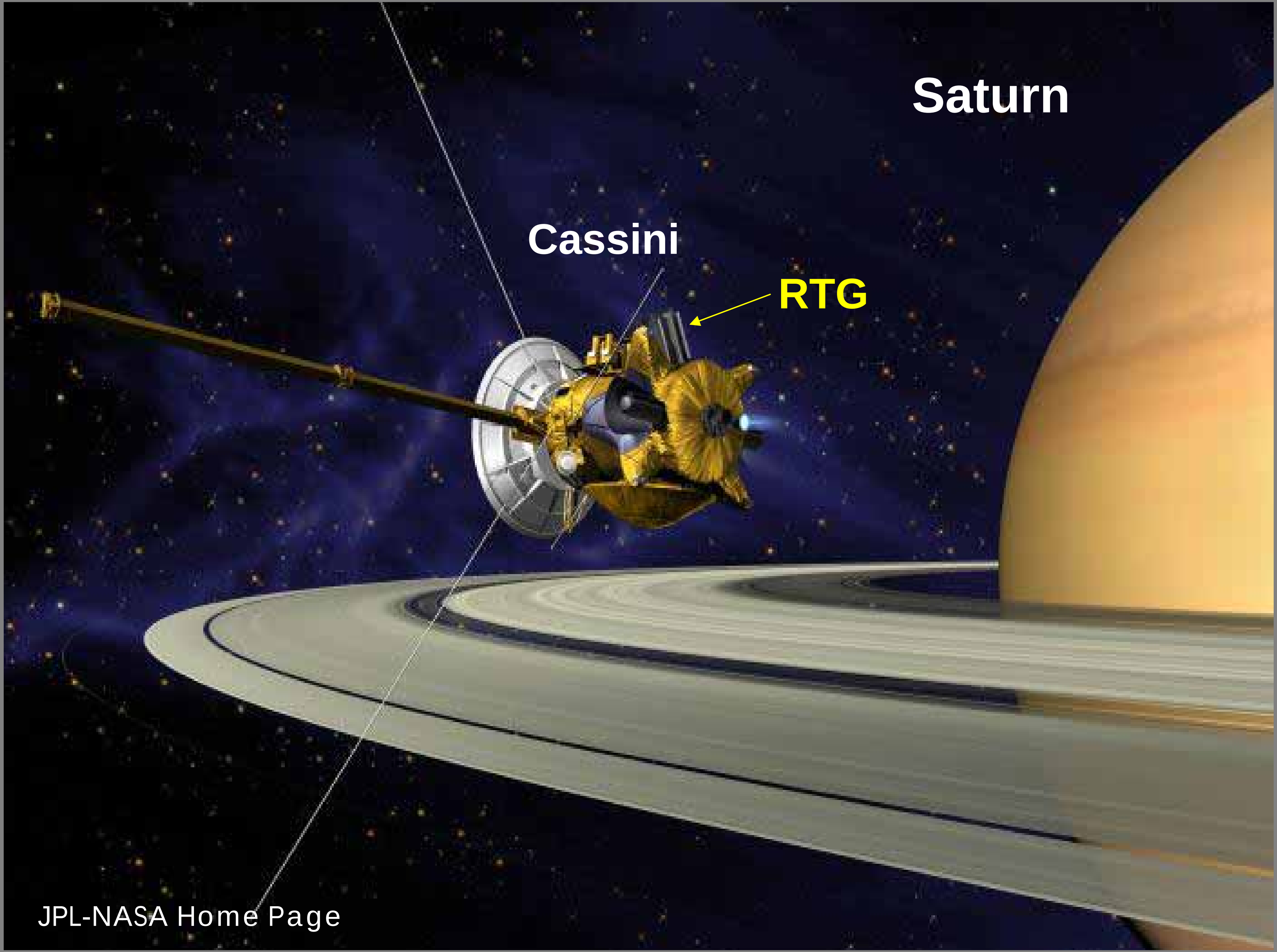
High TE Performance of $Ca_3Co_4O_9$ Thin Film

K. Sugiura et al., *Appl. Phys. Lett.*, **89**, 032111 (2006).





	CCO/film	Bi_2Te_3/bulk	STO/SL
PF(σS^2) @300K($\times 10^{-3}$)	**0.5**	**4.8**	**39**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