New n-Type Thermoelectric Oxides with the Perovskite Structure

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UK Thermoelectric Network Meeting

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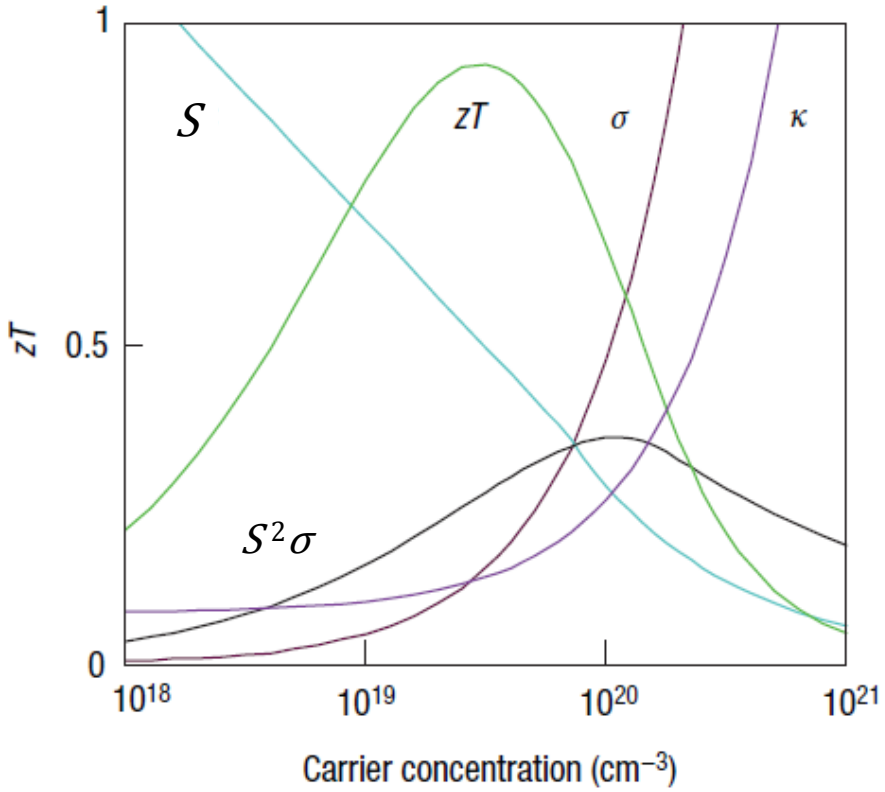
Thermoelectrics



*m** – carrier effective mass
n – carrier concentration
μ – carrier mobility
L – Lorenz factor (2.4×10^{-8} $J^2 K^{-2} C^{-2}$)
C_v – heat capacity
l_{ph} – phonon mean free path
v_s – mean velocity of sound (phonons)

Figure of merit:

$$ZT = \frac{S^2\sigma}{\kappa} T$$

Seebeck (for metals or semiconductors):

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

Electronic conductivity:

$$\sigma = ne\mu$$

Thermal conductivity:

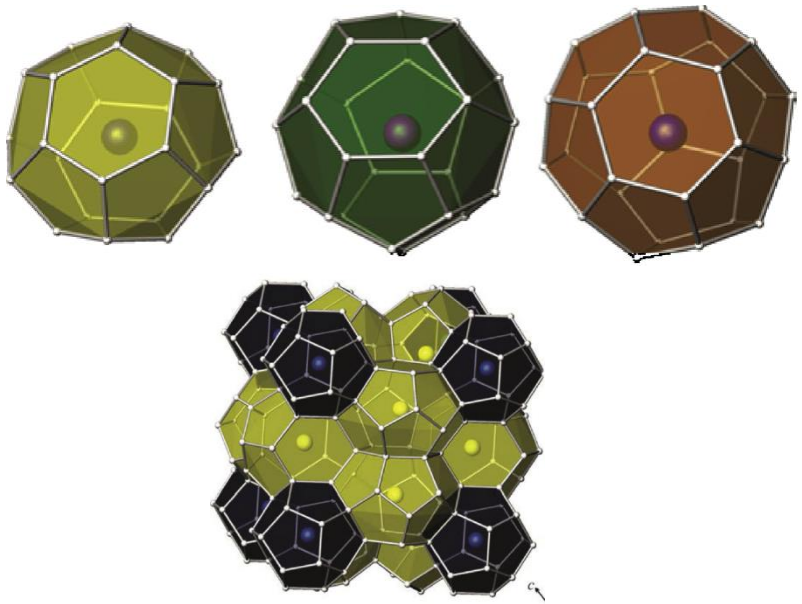
$$\kappa_{total} = \kappa_{elec} + \kappa_{latt}$$

where:

$$\kappa_{elec} = L\sigma T \quad \text{and} \quad \kappa_{latt} = \frac{1}{3} C_V l_{ph} v_s$$

Snyder *et al.*, *Nature Materials*, **7** (2008), 105

Phonon glass electron crystals



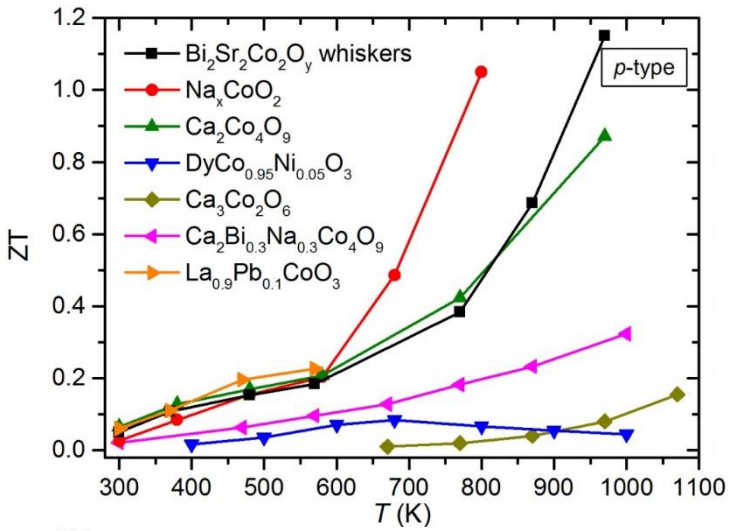
- Clathrates and skutterudites with framework structures containing guest cations.
- Loosely-bound "rattler" guest atoms lead to reduction of phonon velocities and therefore thermal conductivity.
- This does not inhibit electronic transport which is mediated through covalent framework.

Reducing intrinsic thermal conductivity:

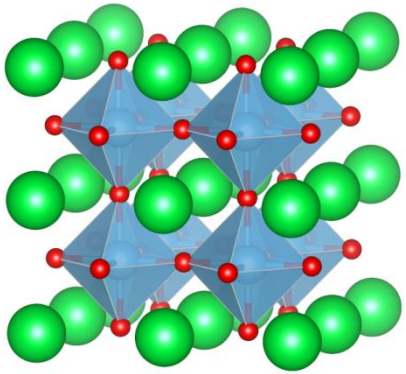
- Increased structural complexity
  - Large unit cell
  - High molecular weight
  - Layering/superlattices
- Disorder within the unit cell
  - Mass/strain disorder through alloying
  - Rattler effects
- Chemical bonding
  - Strong anharmonicity
  - Soft chemical bonding

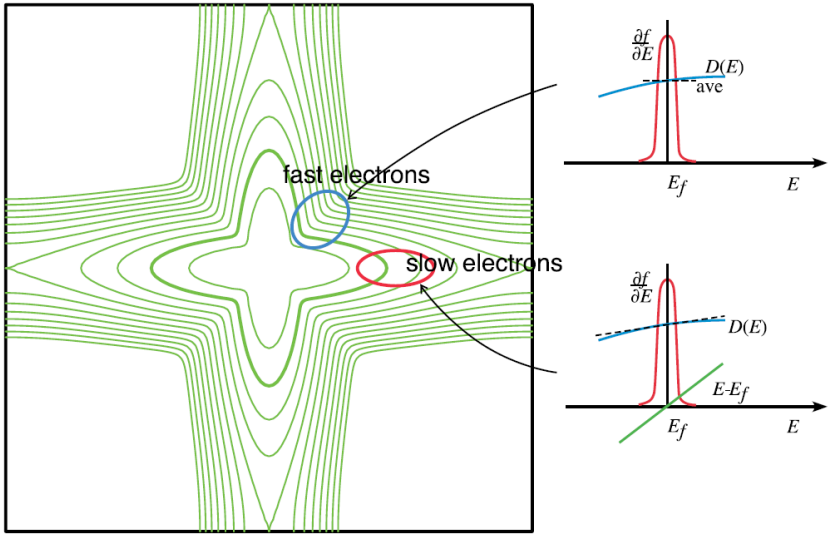
Dolyniuk *et al.*, *Mater. Sci. Eng. R*, **108** (2016), 1

Oxides



- Titanates have unique electronic structures with multiple carriers resulting from high symmetry of crystal structure





Shirai *et al.*, *J. Appl. Phys.*, **113** (2013), 053705

Titanates

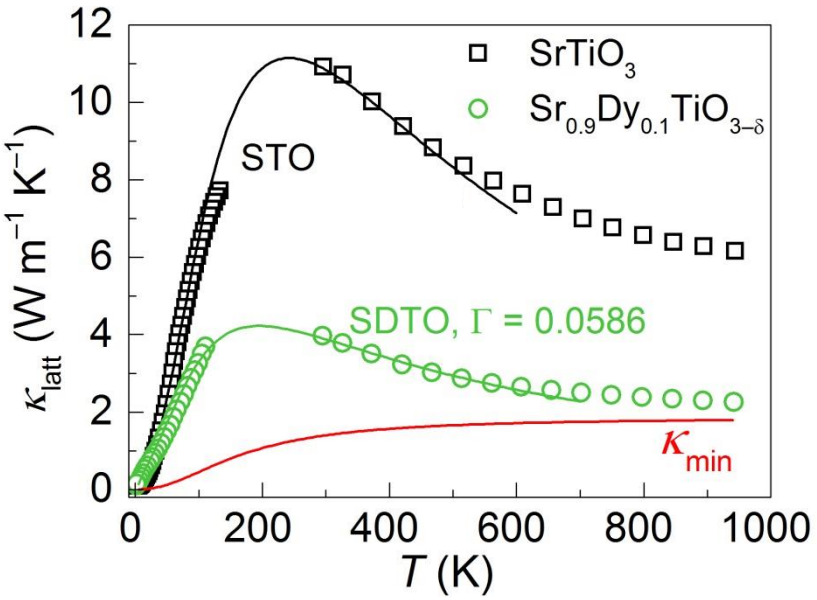
Lattice contribution dominant in oxides and is proportional to phonon mean free path (l_{ph}):

$$\kappa_{latt} = \frac{1}{3} C_V l_{ph} v_s$$

Phonon mean free path is directly proportional to phonon relaxation time (τ)

Matthiessen's rule for scattering mechanism contributions to total thermal resistance:

$$\tau_{ph}^{-1} = \tau_B^{-1} + \tau_{pd}^{-1} + \tau_U^{-1} + \tau_{LI}^{-1} + \tau_{res}^{-1}$$



Material	Γ_{MF}	$\kappa_{300\ K}$
$Sr_{0.9}Y_{0.1}TiO_3$	1.93×10^{-5}	5.50
$Sr_{0.9}Dy_{0.1}TiO_3$	5.58×10^{-2}	4.50
$Sr_{1-x}La_{0.67x}\square_{0.33x}TiO_3$, x=0.8	0.404	2.50
$La_{0.5}Na_{0.5}TiO_3$	0.513	?

Phonon relaxation time due to point defect scattering:

$$\tau_{pd}^{-1} = \frac{V\omega^4}{4\pi v_p^2 v_g}\left(\underbrace{\sum_i f_i\left(1-\frac{m_i}{\bar{m}}\right)^2}_{\text{Mass term } \Gamma_{MF}} + \underbrace{\sum_i f_i\left(1-\frac{r_i}{\bar{r}}\right)^2}_{\text{Size term } \Gamma_{SF}}\right)$$

Point defect scattering

Cation substitution:

- STO and SDTO both display phonon-crystal characteristics
  - typical T^{-1} dependence of κ at high temperatures
- Experimental data of STO and SDTO reproduced well by modified Callaway model for crystalline materials
- Γ_{MF} of LNTO contributes 99.9% of total Γ parameter
  - Γ_{SF} contribution is negligible
- Introduction of high-mass contrast "disorder" through A site substitution reduces κ by 80% at room temperature.

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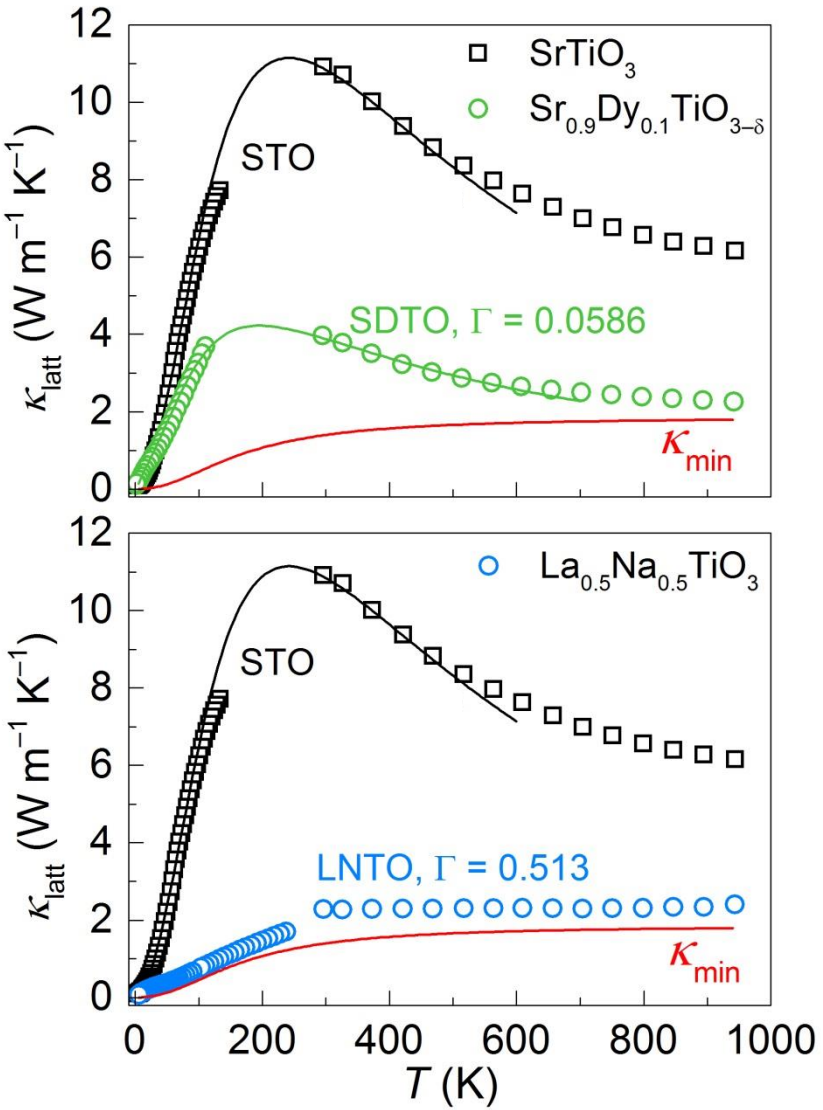
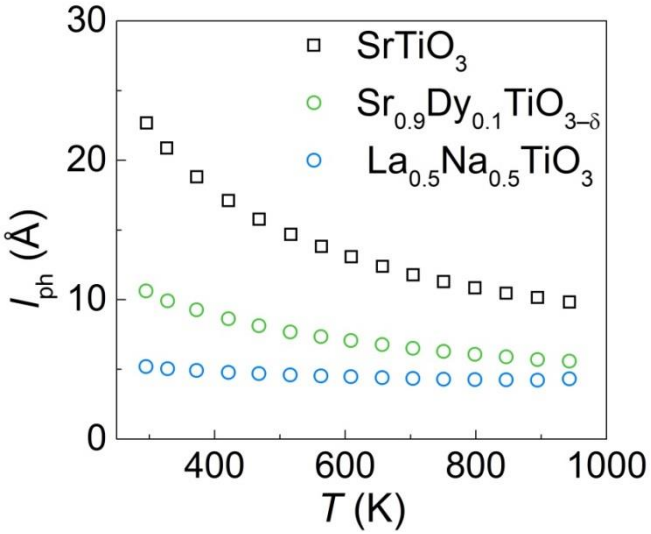


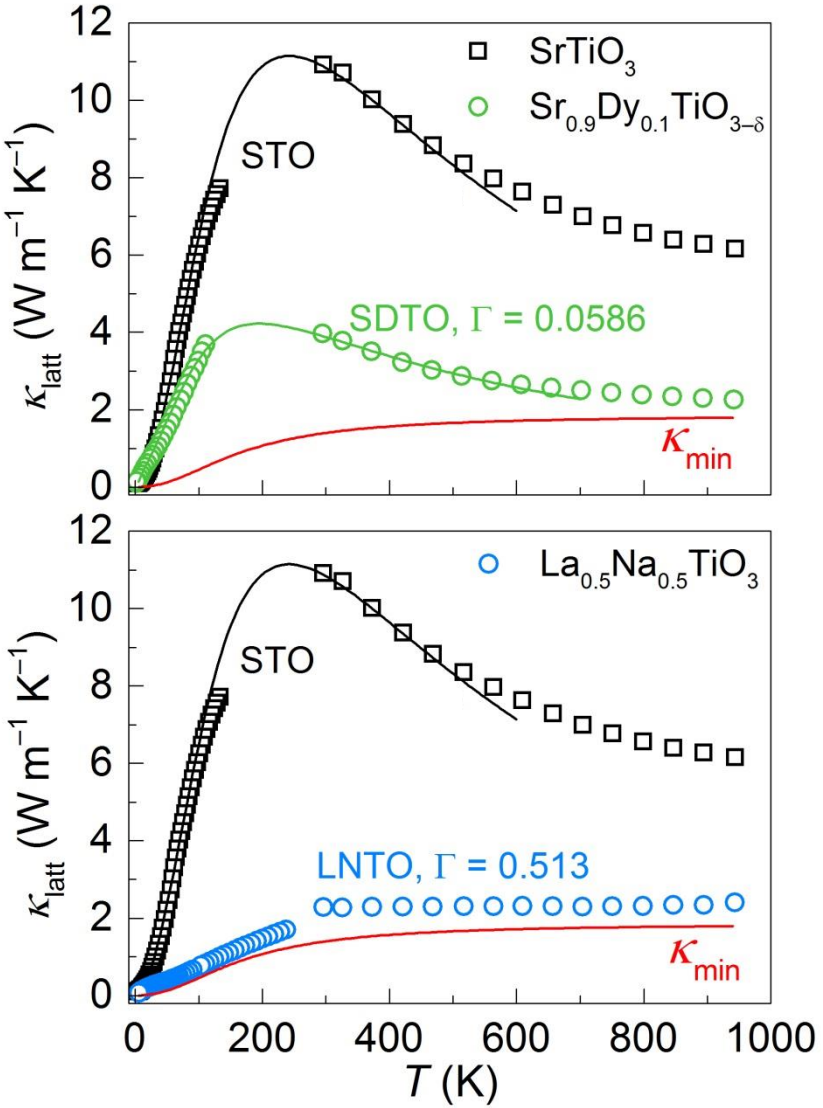
Daniels and Savvin *et al.*, *Energy Environ. Sci.*, **10** (2017), 1917

Phonon mean free path

Cation substitution:

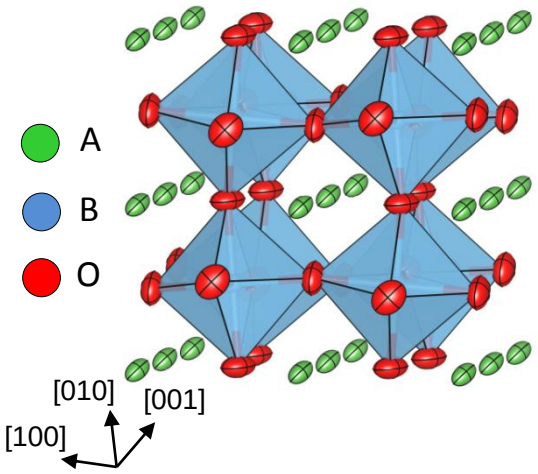
- Constant κ of LNTO above room temperature
- Close comparison against theoretical minimum (κ_{min}) given by Cahill model for disordered solids
- Constant phonon MFP as function of T for LNTO due to vibrations localised over interatomic distances

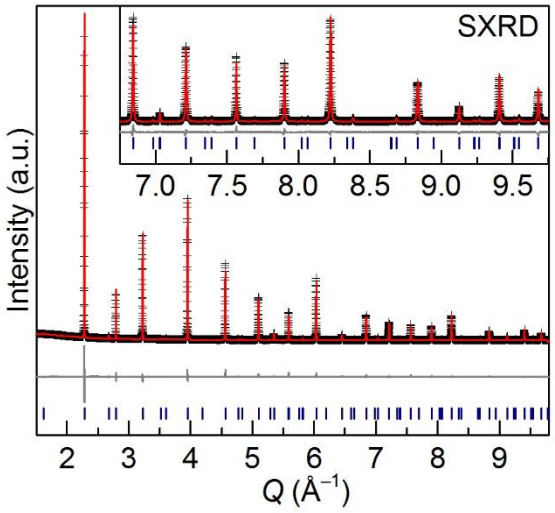


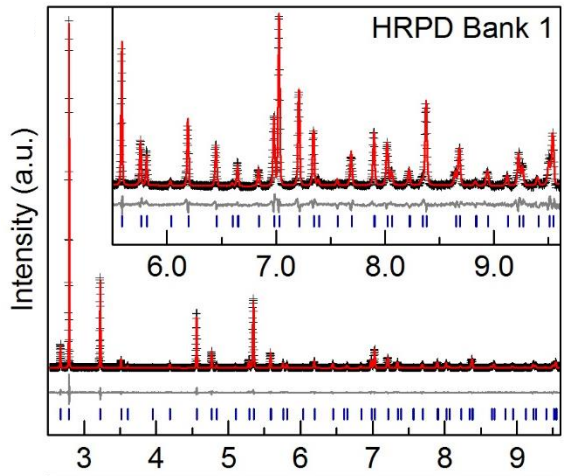


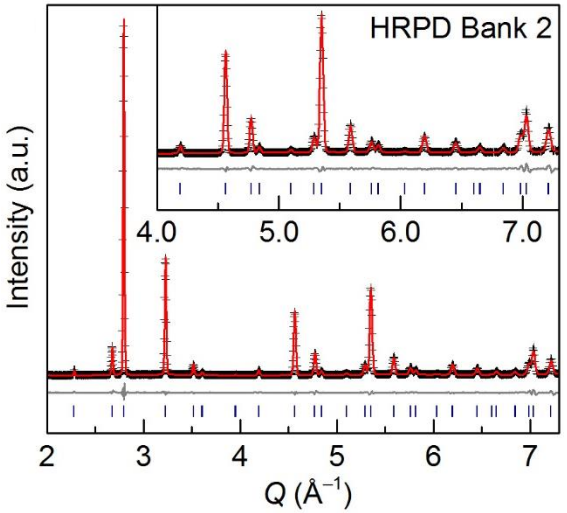
Daniels and Savvin *et al.*, *Energy Environ. Sci.*, **10** (2017), 1917

A site disorder







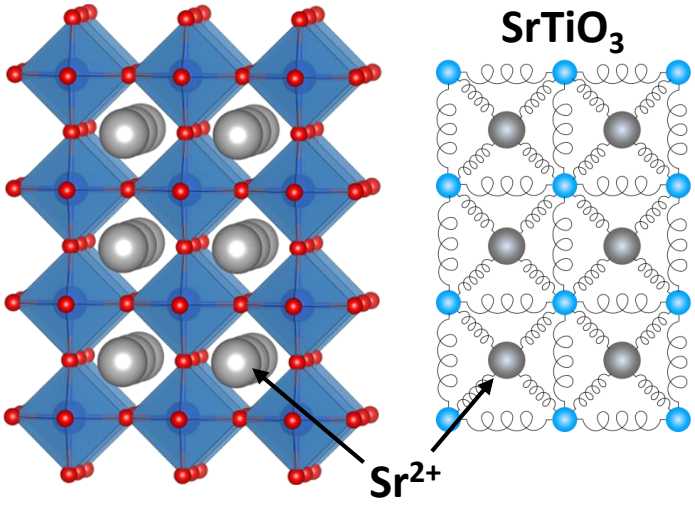


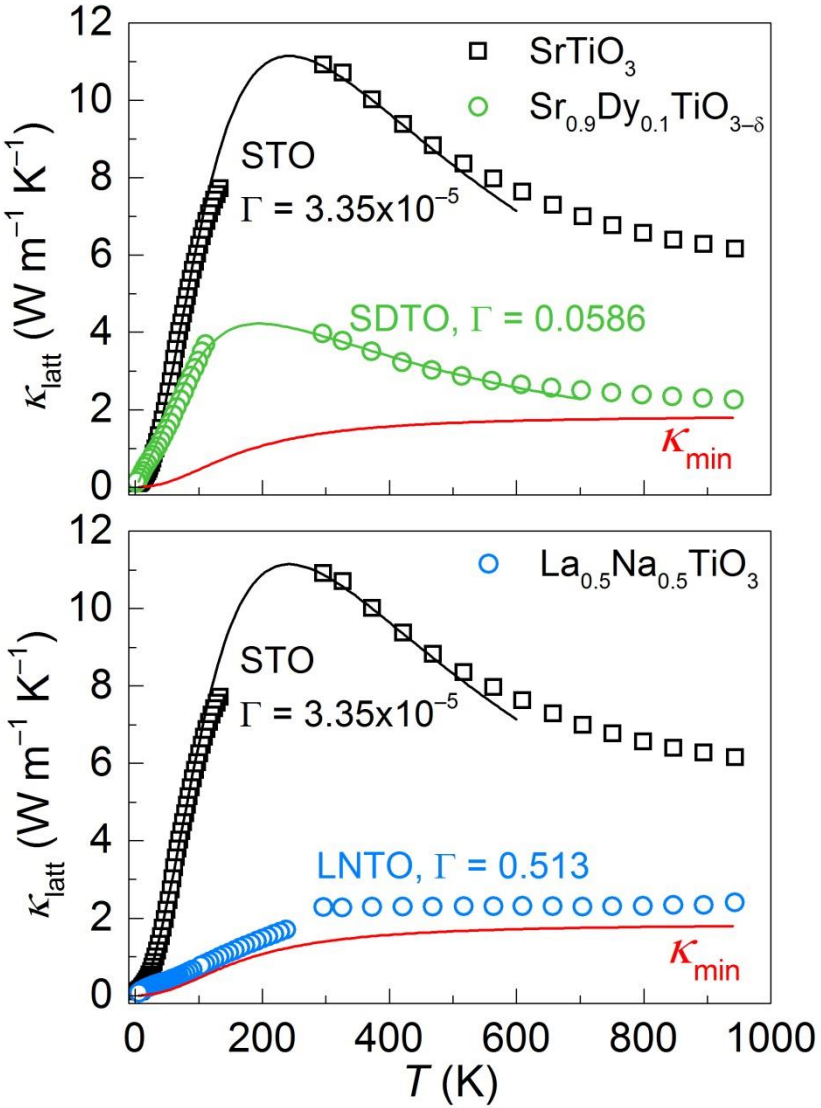
Cation disorder:

- Despite glassy κ, material is perfectly crystalline
- A site cations disordered across the site
- Glassy behaviour of κ arises from random distribution of high-mass contrast cations
- Yields phonon-glass crystalline properties

Daniels and Savvin *et al.*, *Energy Environ. Sci.*, **10** (2017), 1917

Phonon glass $La_{0.5}Na_{0.5}TiO_3$





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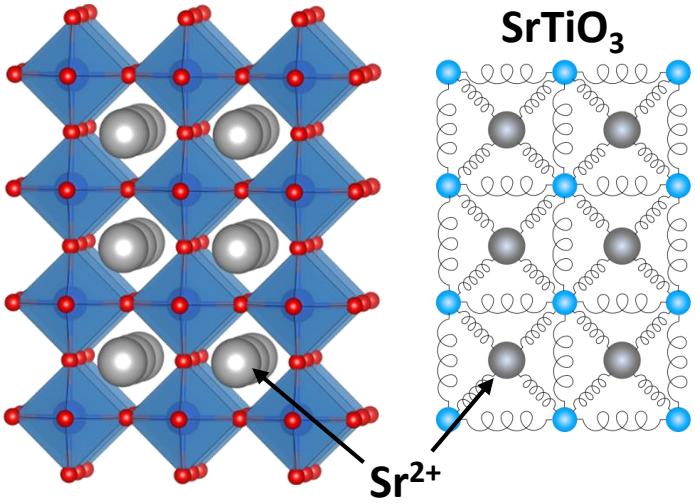

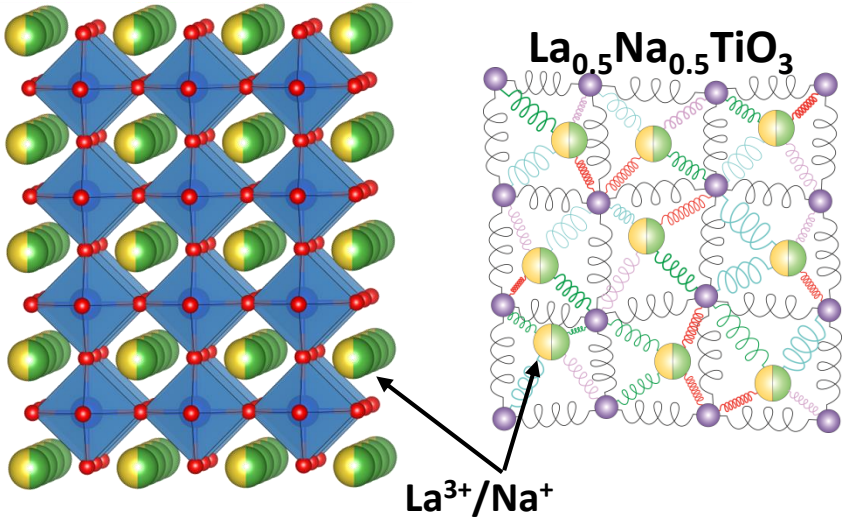

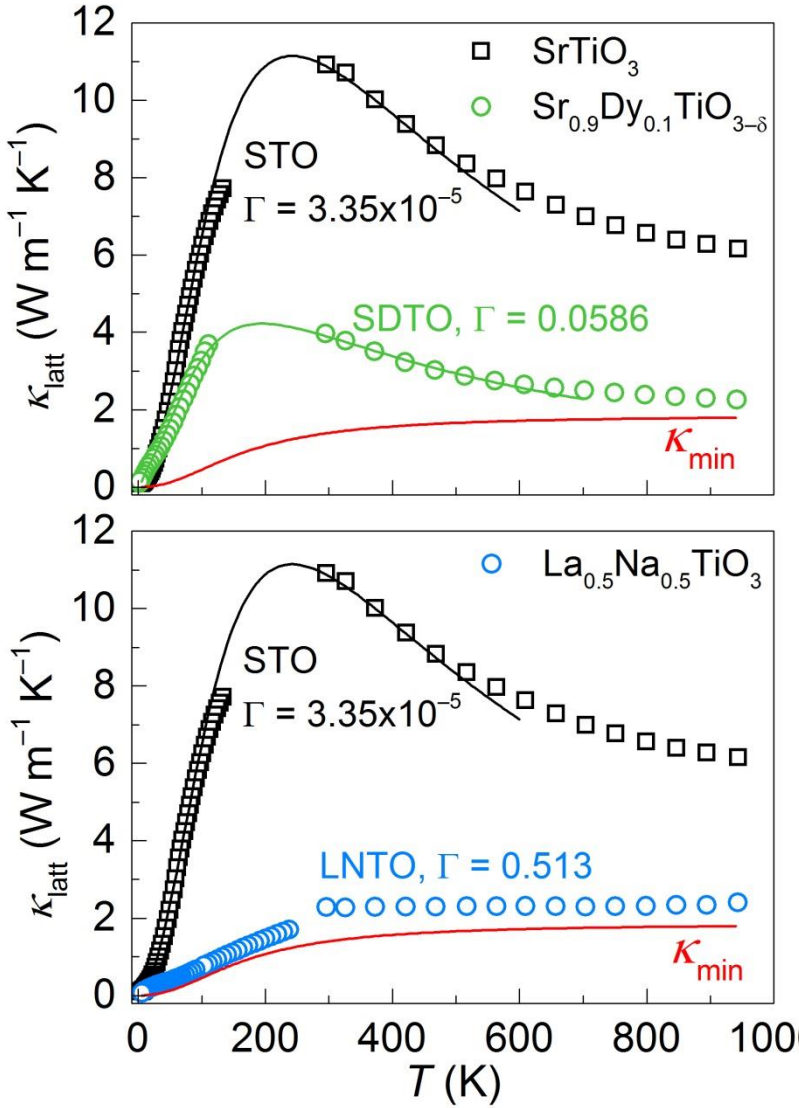

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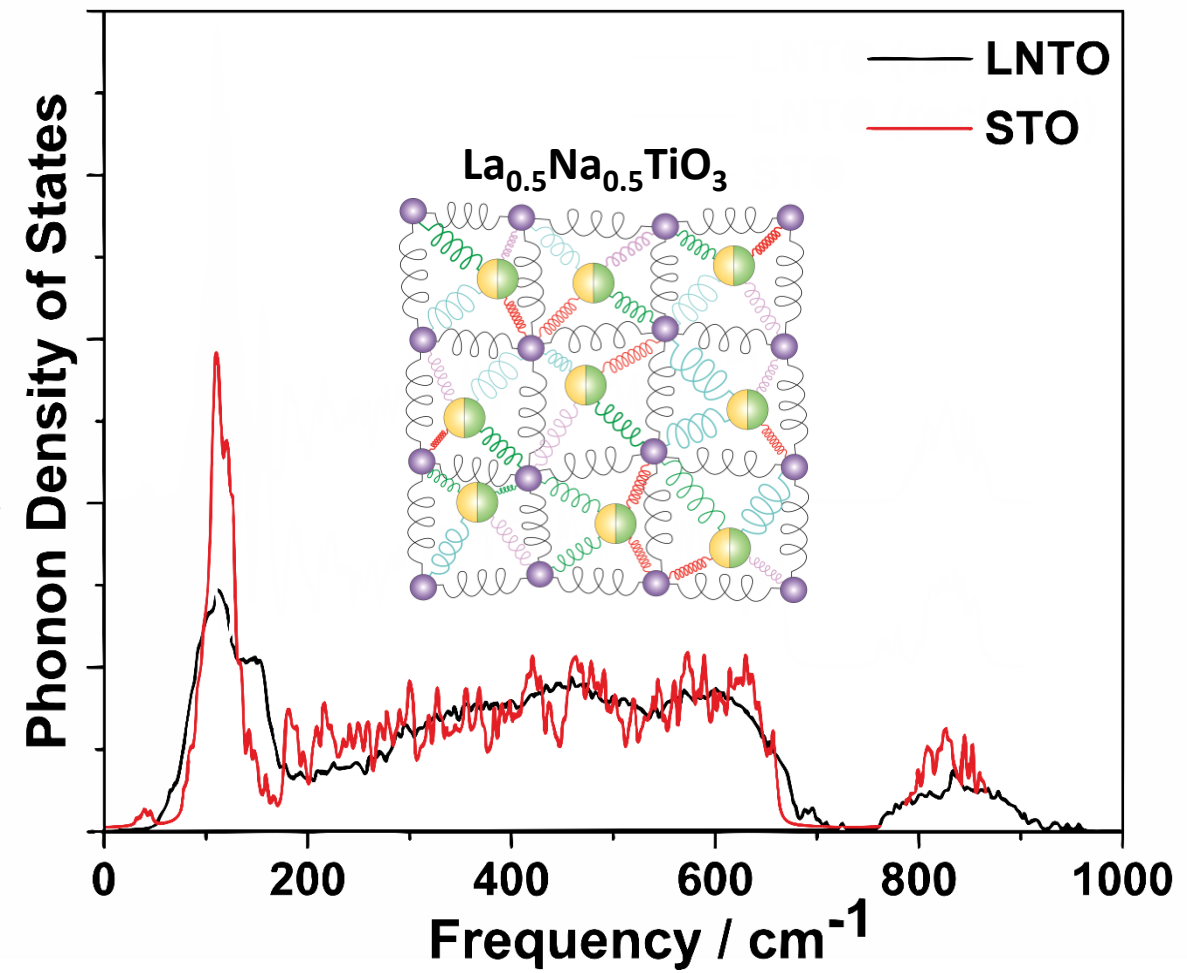
Static DFT calculations

Phonon density of states:

- Low frequency region (<300 cm^{-1}) contributes heavily to thermal conductivity
- Region well defined (narrow) for $SrTiO_3$
- Resonance at ~110 cm^{-1} agrees well with value used in Debye-Callaway model used to describe κ
- A site cation disorder and high mass contrast results in broadened low-frequency region
- Flattening of phonon dispersions similar to clathrates and skutterudites



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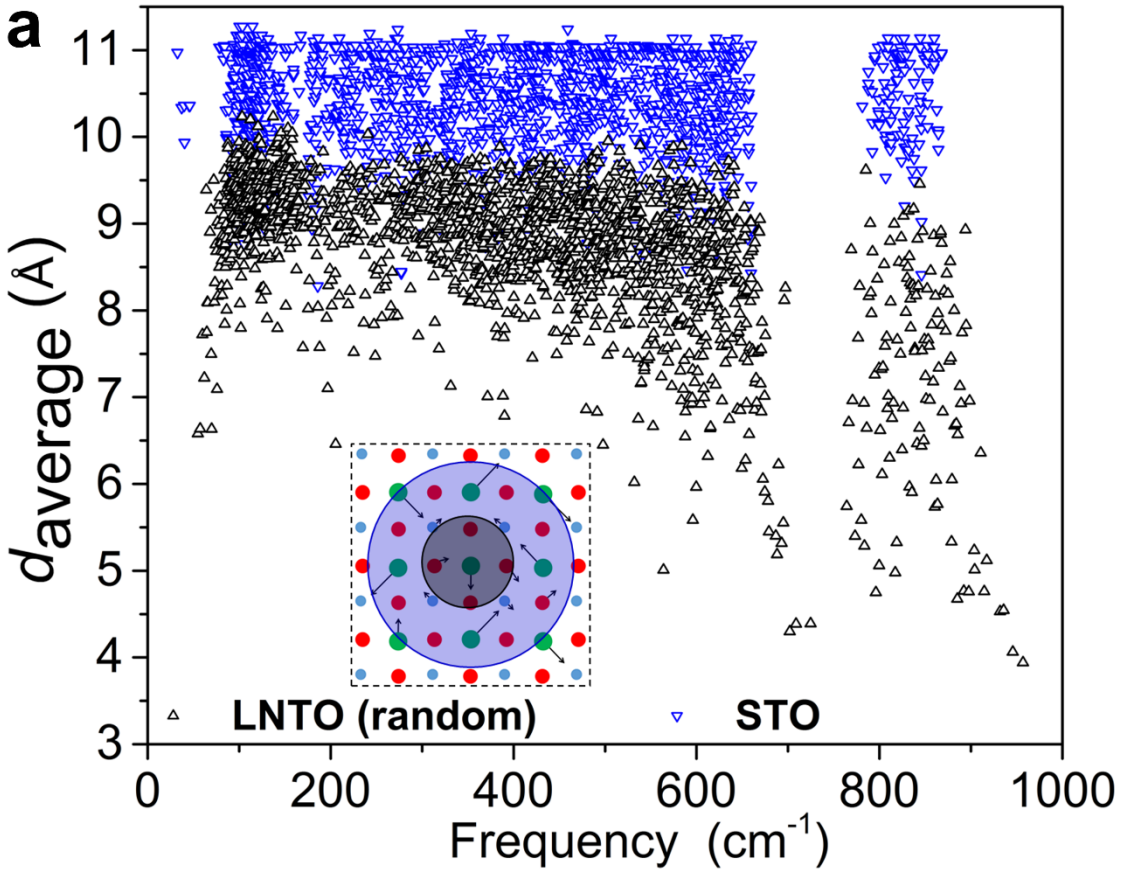
Calculations performed by Dr Sanliang Ling, UCL

Phonon localisation in $La_{0.5}Na_{0.5}TiO_3$

Phonon localisation:

- Computed average separation ($d_{average}$) between 10 atoms exhibiting largest displacements for each phonon mode
- Coherent phonon transport in STO through well-established periodic nearest neighbour couplings
- Phonons are more localised in LNTO as a result of disorder



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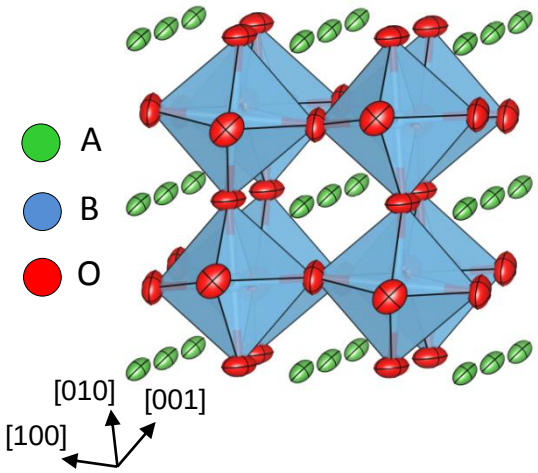
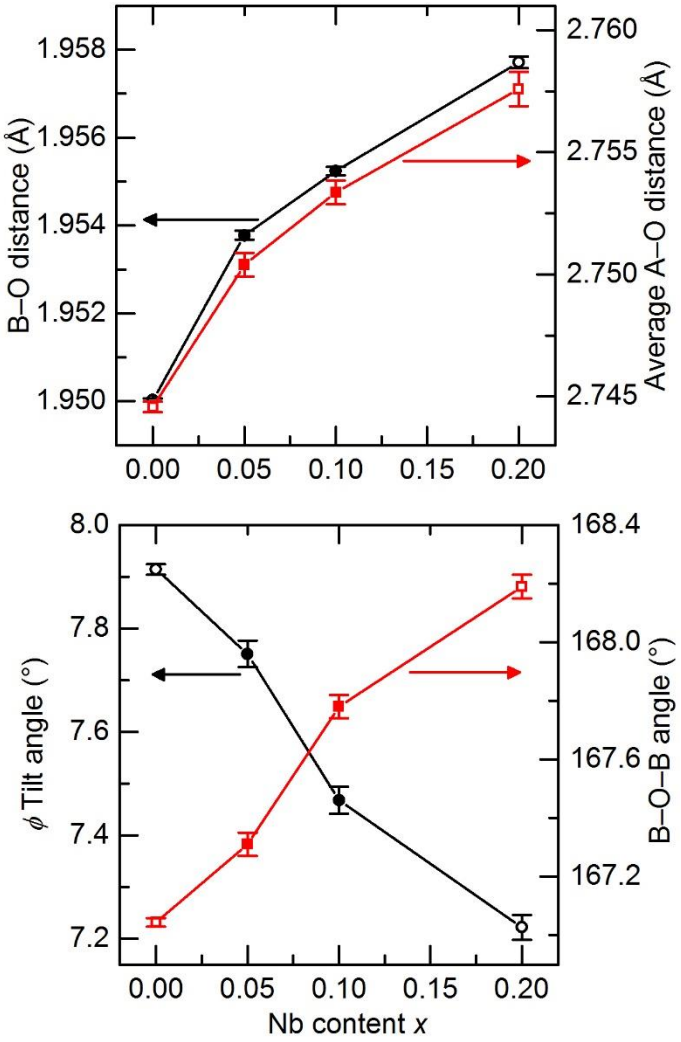
$La_{0.5}Na_{0.5}Ti_{1-x}Nb_xO_3$



B site substitution:

- LNTO is hexagonal with *R*-3*c* symmetry
- Substitution of Nb^{5+} expands unit cell and reduces octahedral tilting



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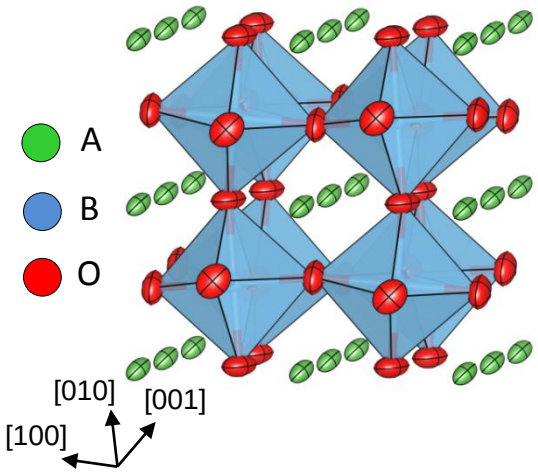
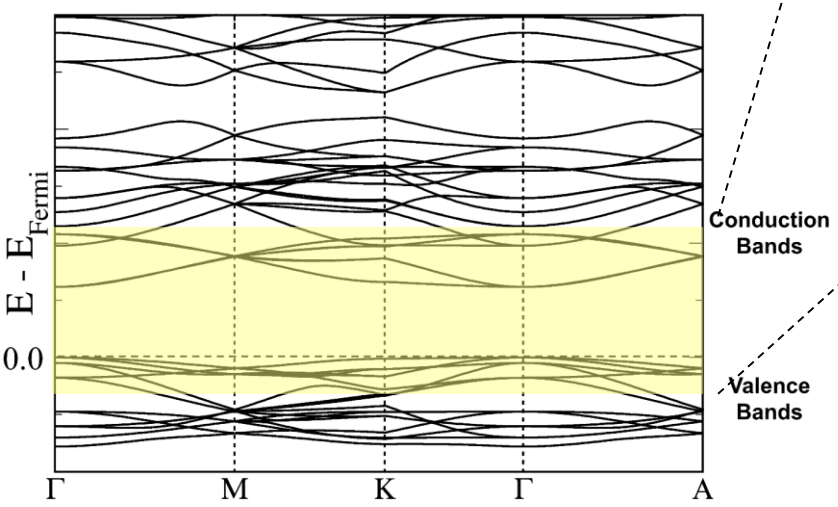
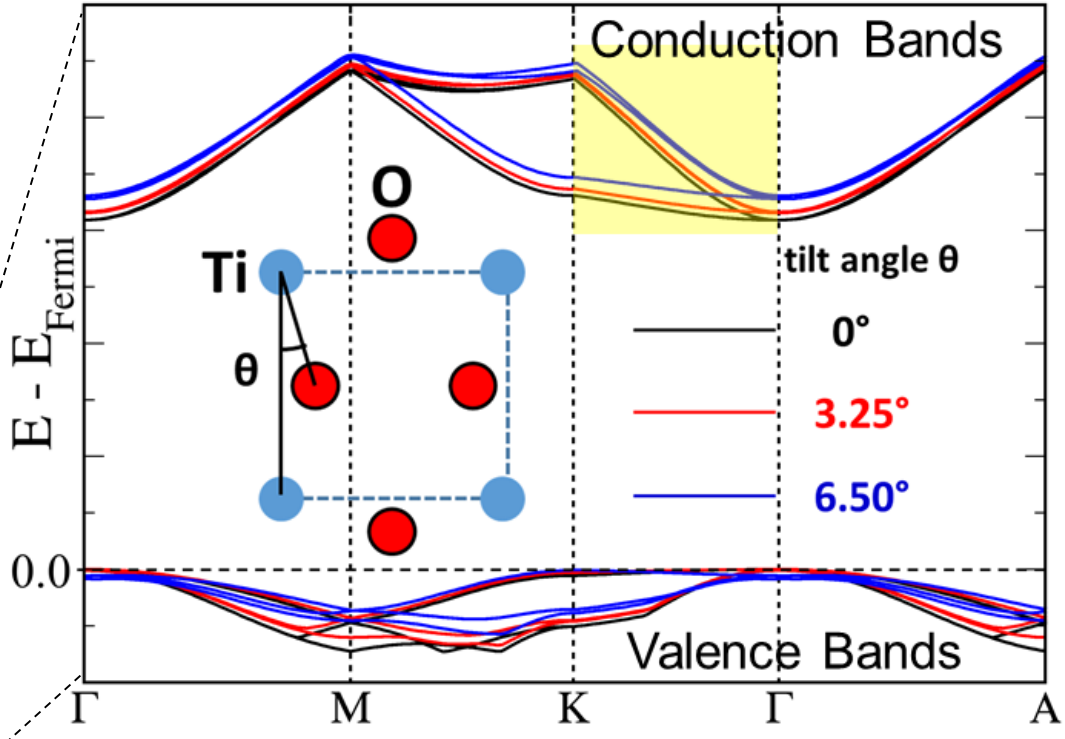
Band structures





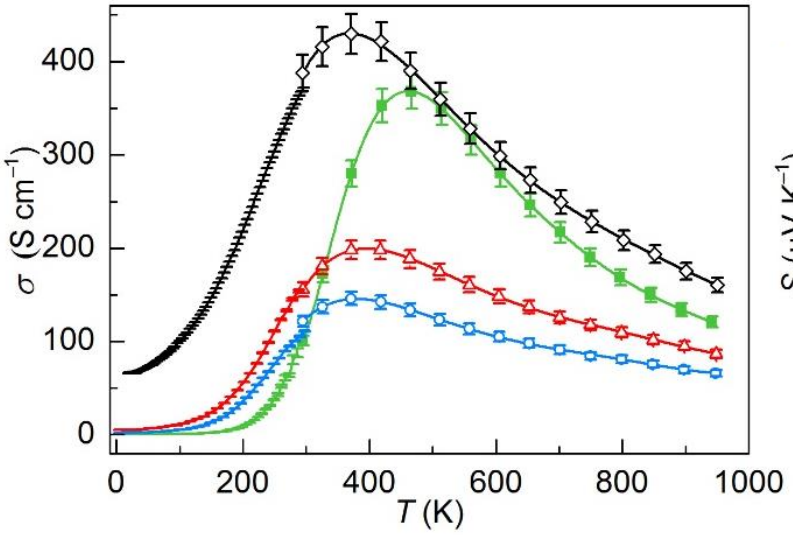


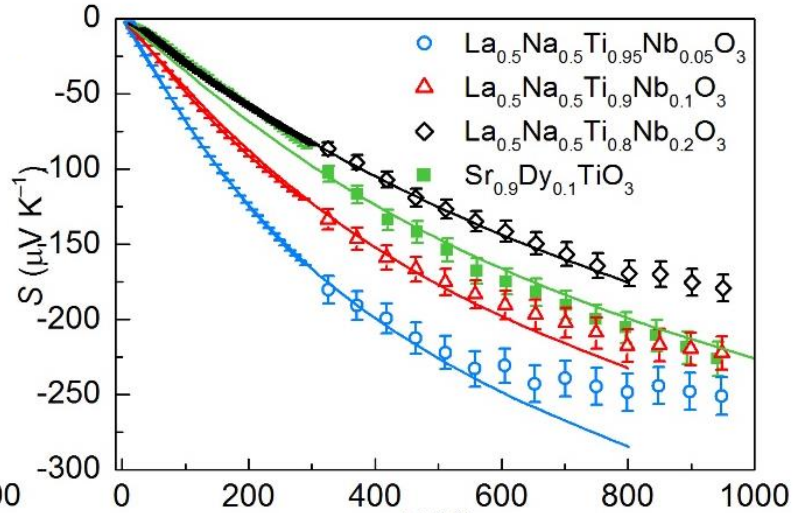
- Coexistence of dispersive and dispersion-less bands at the bottom of the conduction band is retained in LNTO

Daniels and Savvin *et al.*, *Energy Environ. Sci.*, **10** (2017), 1917

Calculations performed by Dr Sanliang Ling, UCL

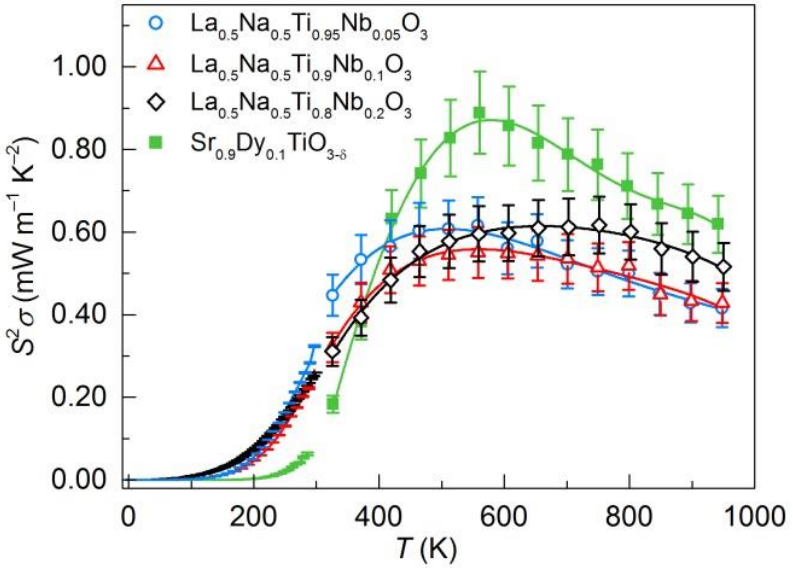
Electronic properties





B site substitution:

- Increasing carrier concentration increases *σ*, but decreases *S*
- Able to extract carrier concentrations through fitting of Seebeck data
- Large grain boundary contributions to *σ* limit the power factor



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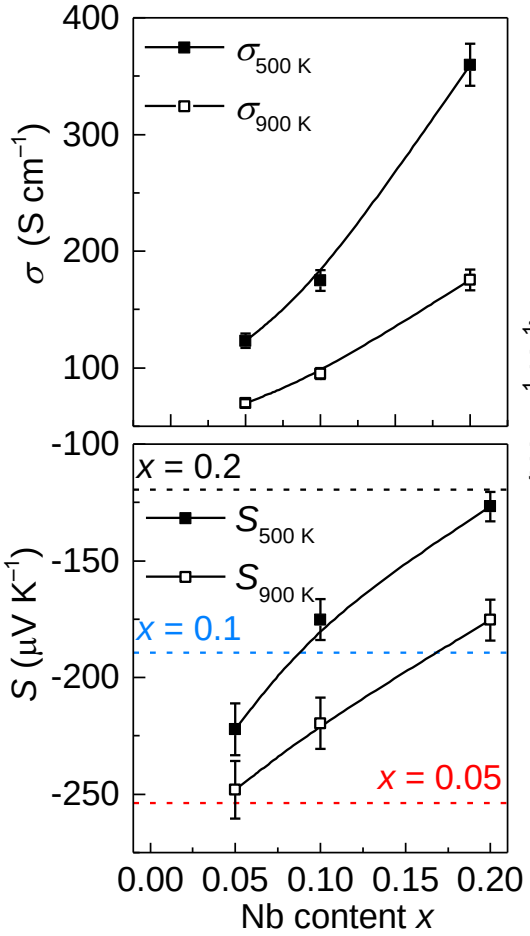

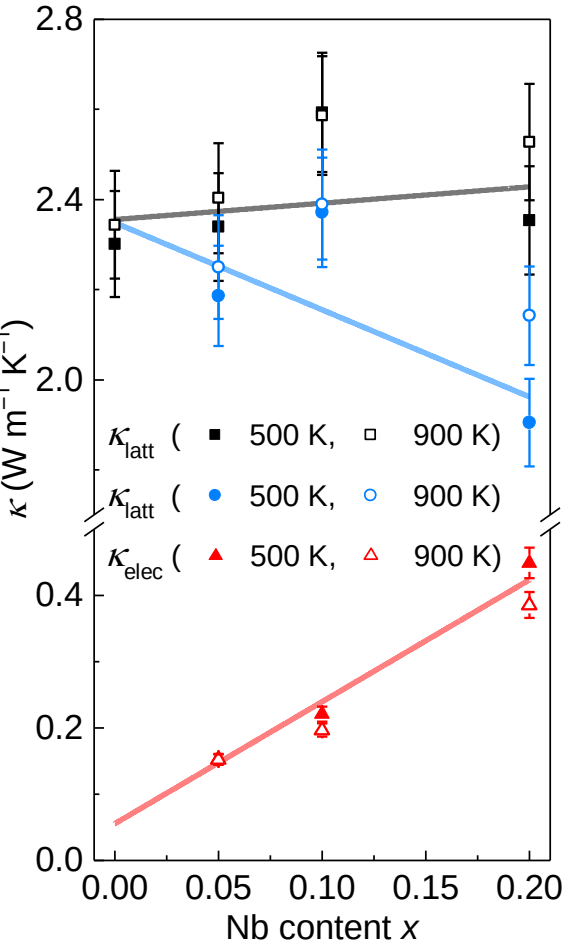

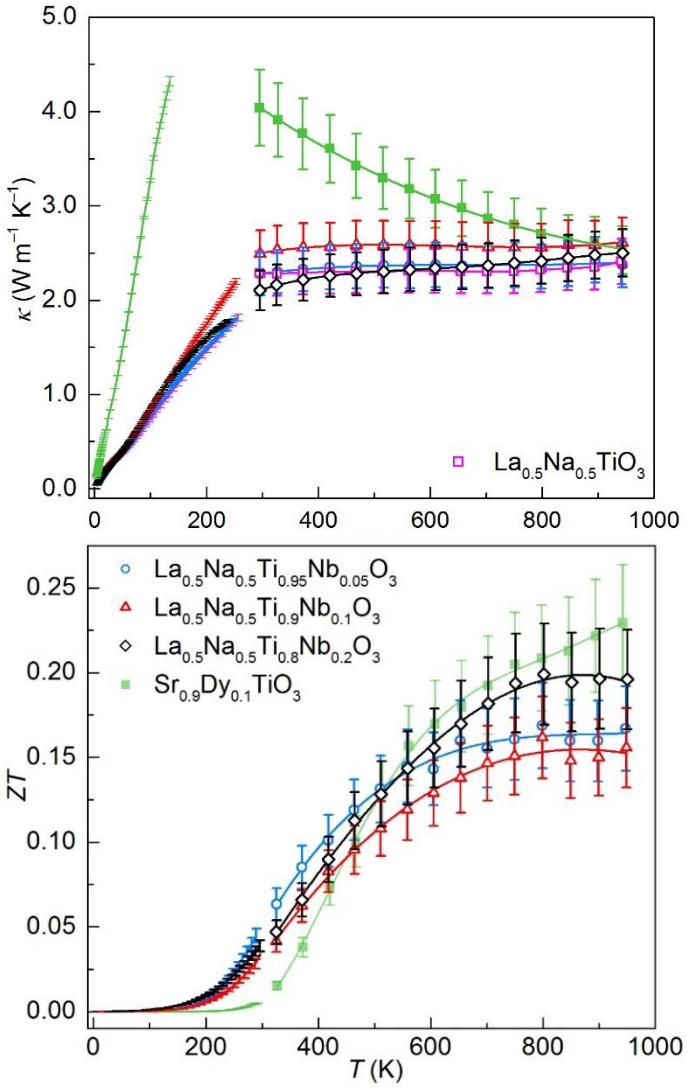

Daniels and Savvin *et al.*, *Energy Environ. Sci.*, **10** (2017), 1917

Conclusions & plans

Conclusions:

- Phonon engineering of $SrTiO_3$ through substitution to $La_{0.5}Na_{0.5}TiO_3$ results in phonon-glass thermal conductivity
- Chemistry of $La_{0.5}Na_{0.5}TiO_3$ analogous to that of $SrTiO_3$, meaning it can be doped either through A or B site
- Phonon-glass thermal conductivity is retained upon B site substitution with donor Nb^{5+} which enhances electronic transport
- Thermal and electronic transport are largely decoupled in $La_{0.5}Na_{0.5}Ti_{1-x}Nb_xO_3$, yielding PGEC characteristics

Future plans:

- Explore high-mass contrast combinations to target other phonon glass systems
- Optimise processing of titanate ceramics to enhance PF further

Acknowledgements

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UCL

Dr Sanliang Ling

Professor Ben Slater

Professor Furio Corà

diamond

Dr Clare Murray

Dr Sarah Day

Science & Technology Facilities Council ISIS

Dr Alexandra Gibbs

Dr Paul Henry