



Advanced Functional Materials for Energy Conversion and Storage

Dr. Zhilun Lu

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About myself

Employment and Education

2021, Lecturer

School of Engineering and the Built Environment, Edinburgh Napier University

2018-2021, Research Associate

Henry Royce Institute, UK (The UK's national institute for advanced materials research and innovation)

2016-2018, Research Scientist

Helmholtz-Zentrum Berlin, Germany (A member of the largest Germany's scientific organisation-Helmholtz Association of German Research Centres)

2011-2016, PhD

Department of Materials Science and Engineering, University of Sheffield (High Quality PhD Thesis Prize).

Academic highlights

Funding

- PI, Royal Society of Chemistry Research Enablement Grant (£9,744) 2022
- PI, Royal Society Research Grant (£19,009) 2022
- Participate in EPSRC-funded projects (~million pounds) 2018-2021

Research

- 58 Journal papers (49 Q1 papers), total impact factor (JCR) – 400+
- Google Scholar: 1300+, h-index 21, i10-index 28
- A top journal review paper (impact factor-60.622)
- Highly cited article by Web of Science (2021)
- Energy and Environmental Science HOT Article (2020)
- Journal of the American Ceramic Society Top Downloaded Paper (2020-2021)
- Journal of the American Ceramic Society Top Downloaded Paper (2018-2019)

CHEMICAL REVIEWS

pubs.acs.org/CR



Review

Electroceramics for High-Energy Density Capacitors: Current Status and Future Perspectives

Ge Wang,[‡] Zhilun Lu,[‡] Yong Li,[‡] Linhao Li, Hongfen Ji, Antonio Feteira, Di Zhou, Dawei Wang,^{*} Shujun Zhang,^{*} and Ian M Reaney^{*}

Energy & Environmental Science



PAPER

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Superior energy density through tailored dopant strategies in multilayer ceramic capacitors†

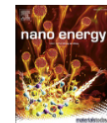
Zhilun Lu,^{‡a,b} Ge Wang,^{‡a,b} Weichao Bao,^{‡c} Jinglei Li,^{‡d} Linhao Li,^{‡a} Ali Mostaed,^{‡ae} Huijing Yang,^{af} Hongfen Ji,^{ag} Dejun Li,^h Antonio Feteira,^{‡i} Fangfang Xu,^{‡c} Derek C. Sinclair,^{‡a} Dawei Wang,^{‡**} Shi-Yu Liu^{†h} and Ian M. Reaney^{‡**}



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journal homepage: <http://www.elsevier.com/locate/nanoen>



Mechanism of enhanced energy storage density in AgNbO₃-based lead-free antiferroelectrics

Zhilun Lu^{a,b,1}, Weichao Bao^{c,1}, Ge Wang^{a,1}, Shi-Kuan Sun^{a,1}, Linhao Li^a, Jinglei Li^d, Huijing Yang^{a,e}, Hongfen Ji^{a,f}, Antonio Feteira^g, Dejun Li^h, Fangfang Xu^c, Annette K. Kleppeⁱ, Dawei Wang^{a,*}, Shi-Yu Liu^{h,*}, Ian M. Reaney^{a,*}

Professional Services

Editorships

Materials Today Communications, Frontiers in Materials, Crystals, Advanced Powder Materials, Journal of Advanced Dielectrics

Memberships

Member of *American Chemical Society (ACS)*

Member of *Royal Society of Chemistry (RSC)*

Member of *Institute of Materials, Minerals & Mining (IOM3)*

Invited Talks

7 keynote speeches and 7 invited talks

Journal reviewer

Physical Review Letters, Acta Materialia, Chemistry of Materials, Scripta Materialia, Nature Scientific Reports, etc

Some concepts

The universe is all of **space** and **time** and their contents



3 dimension, point (0), line (1), face (2D),
cube (3D)

1 dimension, continued, irreversible

Amorphous solid

- Short-range order

Crystalline solids

- Periodicity
- Symmetric
- Long-range order

Types of Materials

Structure

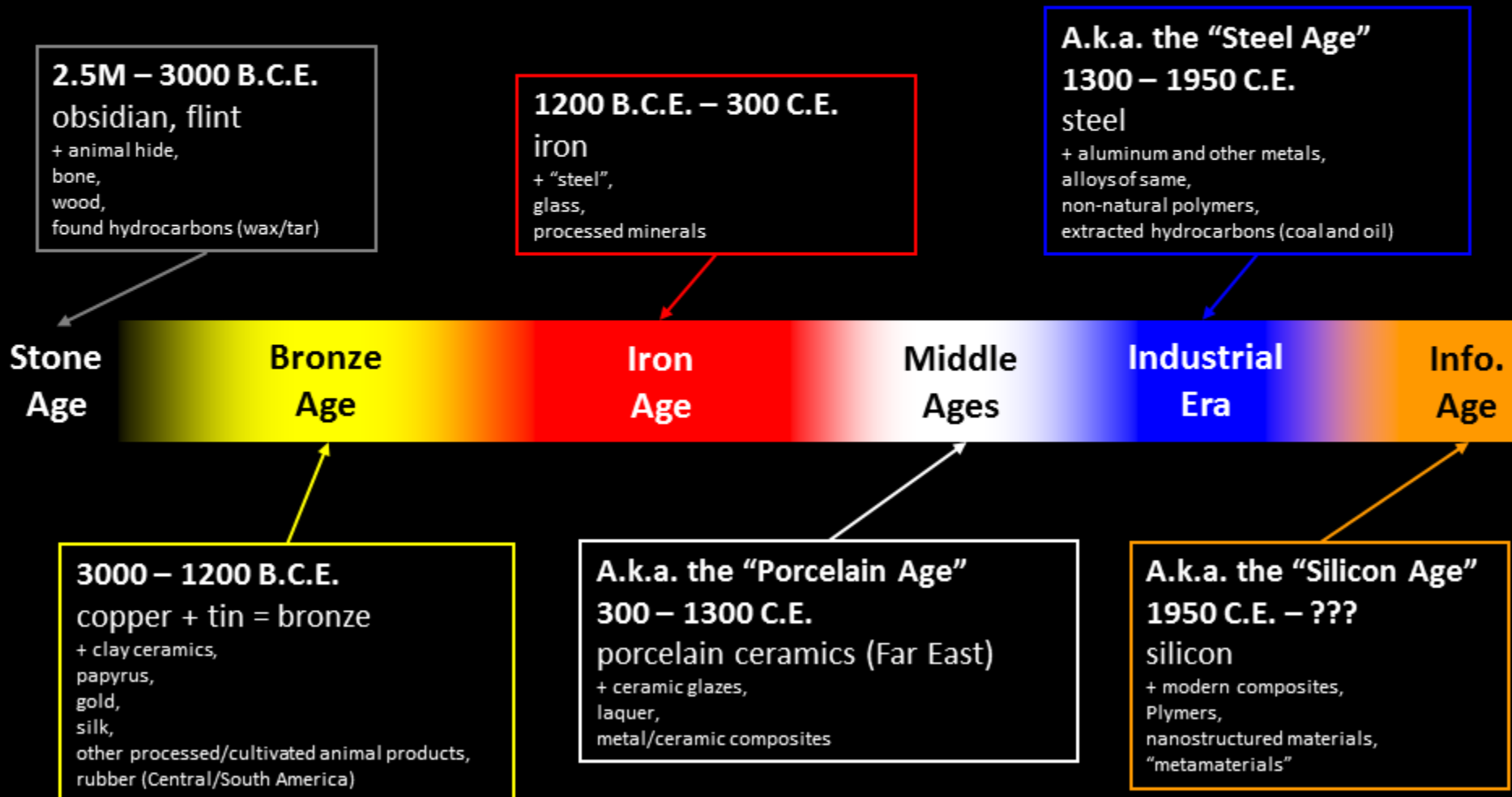
- Metal
- Ceramic and glass
- Polymer
- Composite

Properties

- Mechanical, Strength, Stiffness, Toughness, Ductility, Brittleness, Hardness, Elasticity, etc.
- **Electrical**
- **Thermal**
- **Magnetic**
- Optical

Materials Development by Era

Different eras in human history* are named after the materials incorporated in the predominant technologies



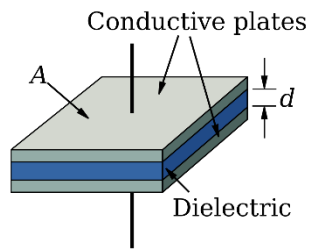
My research

- **Dielectric materials for energy storage capacitors**
- **Thermoelectric oxides for energy conversion and harvesting**
- **Advanced characterization technique-neutron scattering**

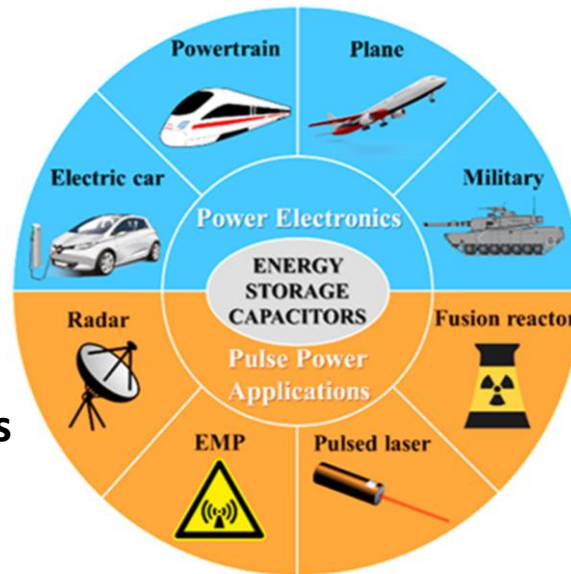
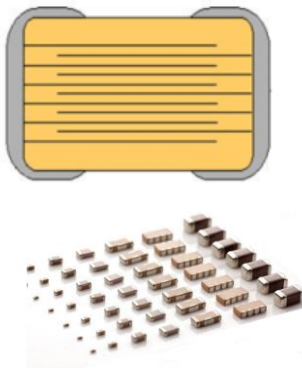
Dielectric materials for energy storage capacitors

Capacitors: Important electrical energy-storage devices for sustainable development

Parallel-plate capacitor

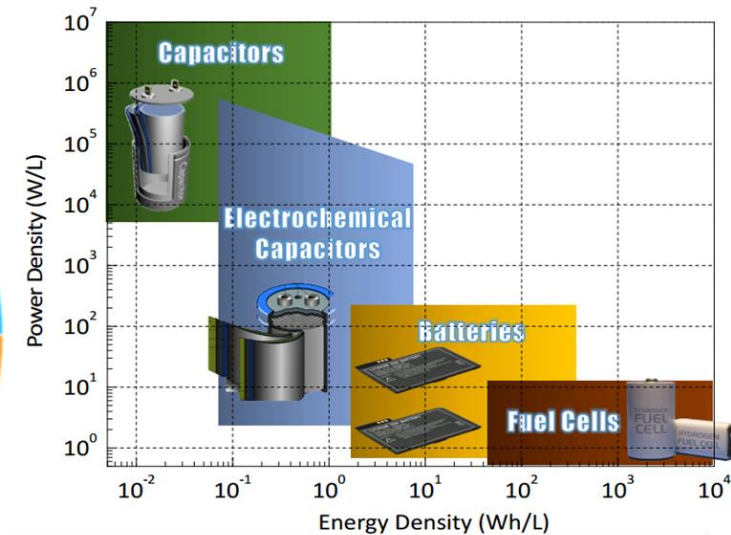


Multilayer ceramic capacitors (MLCC)



Advantages:

- High power density
- High charge/discharge rates
- High voltage
- High reliability



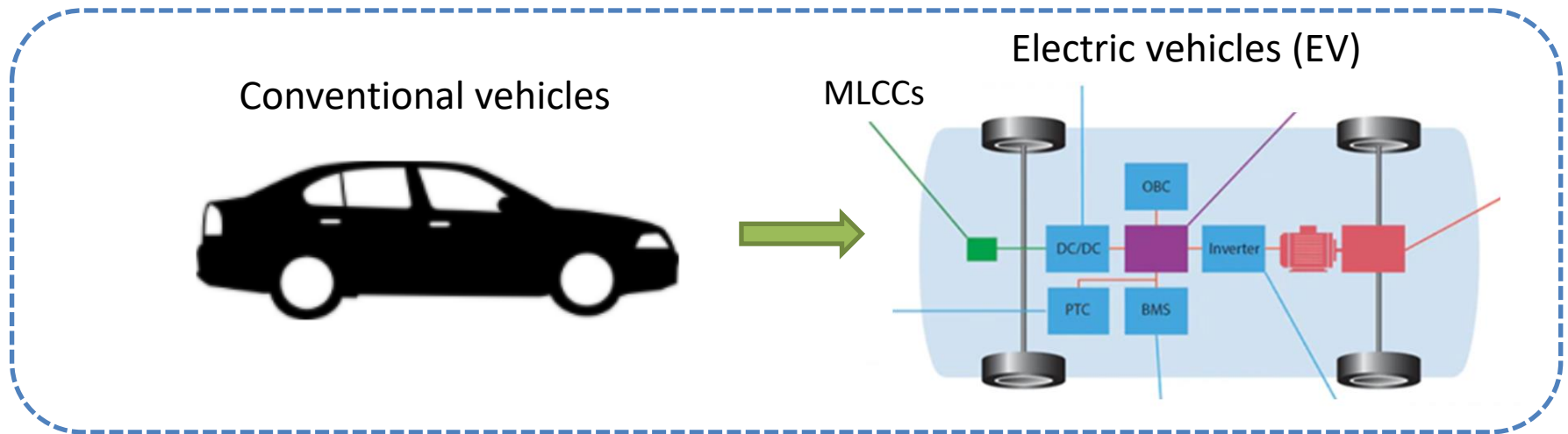
Challenge:

Low energy density

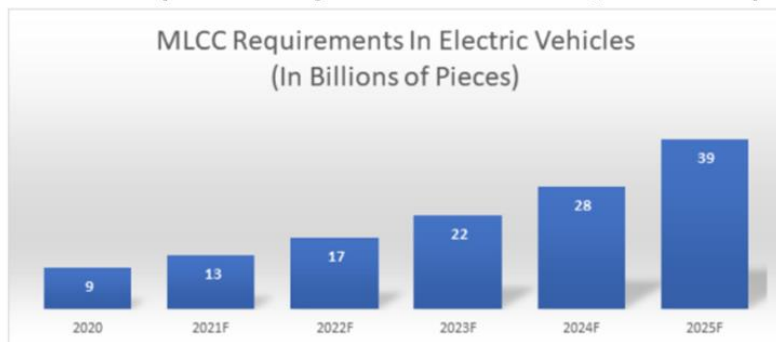
Vision: Accelerating future of mobility

-Developing high energy density capacitors for electric vehicles

Future of mobility: Ambition for all new vehicles to be effectively **zero emission** by 2040



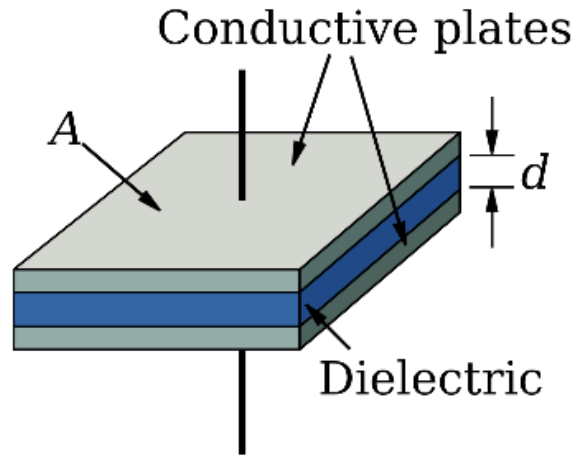
MLCC (Multi-layer ceramic capacitors)



New requirements:

- Higher energy density
 - Smaller size
- Larger capacity
— Higher voltage

How to Enhance the Energy Density of Capacitors?



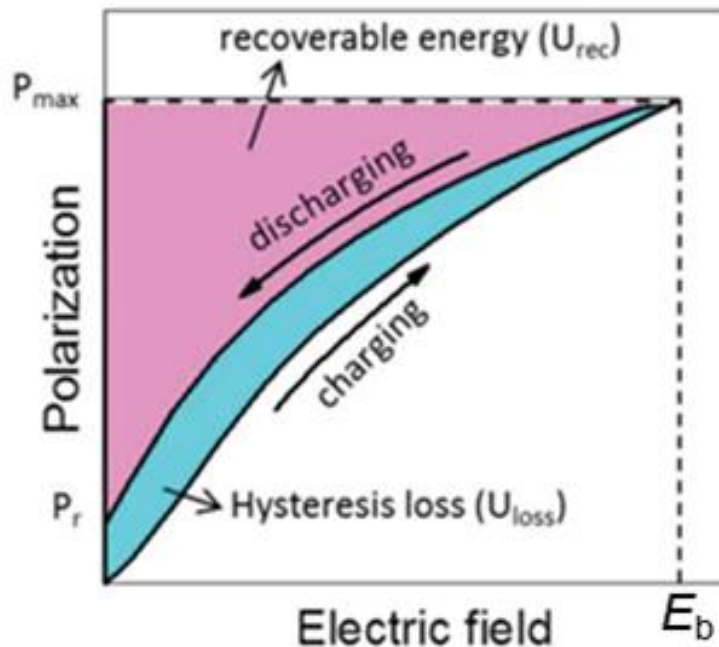
$$C = \epsilon_0 \epsilon_r \frac{A}{d}$$

$$W = \frac{1}{2} QV = \frac{1}{2} CV^2 = \frac{1}{2} \epsilon_0 \epsilon_r \frac{A}{d} V^2$$

$$A \uparrow \quad \epsilon_r \uparrow \quad d \downarrow \quad V \uparrow \quad \longrightarrow \quad W \uparrow$$

Polarization and Breakdown Strength (E_b) — related to ϵ_r and V

- The area to the left of the curve represents (the purple section).
- P_{\max} and P_r are the maximum polarization and the remanent polarization under an applied electric field (E), respectively.



$$U = \int_0^{P_{\max}} E dP$$

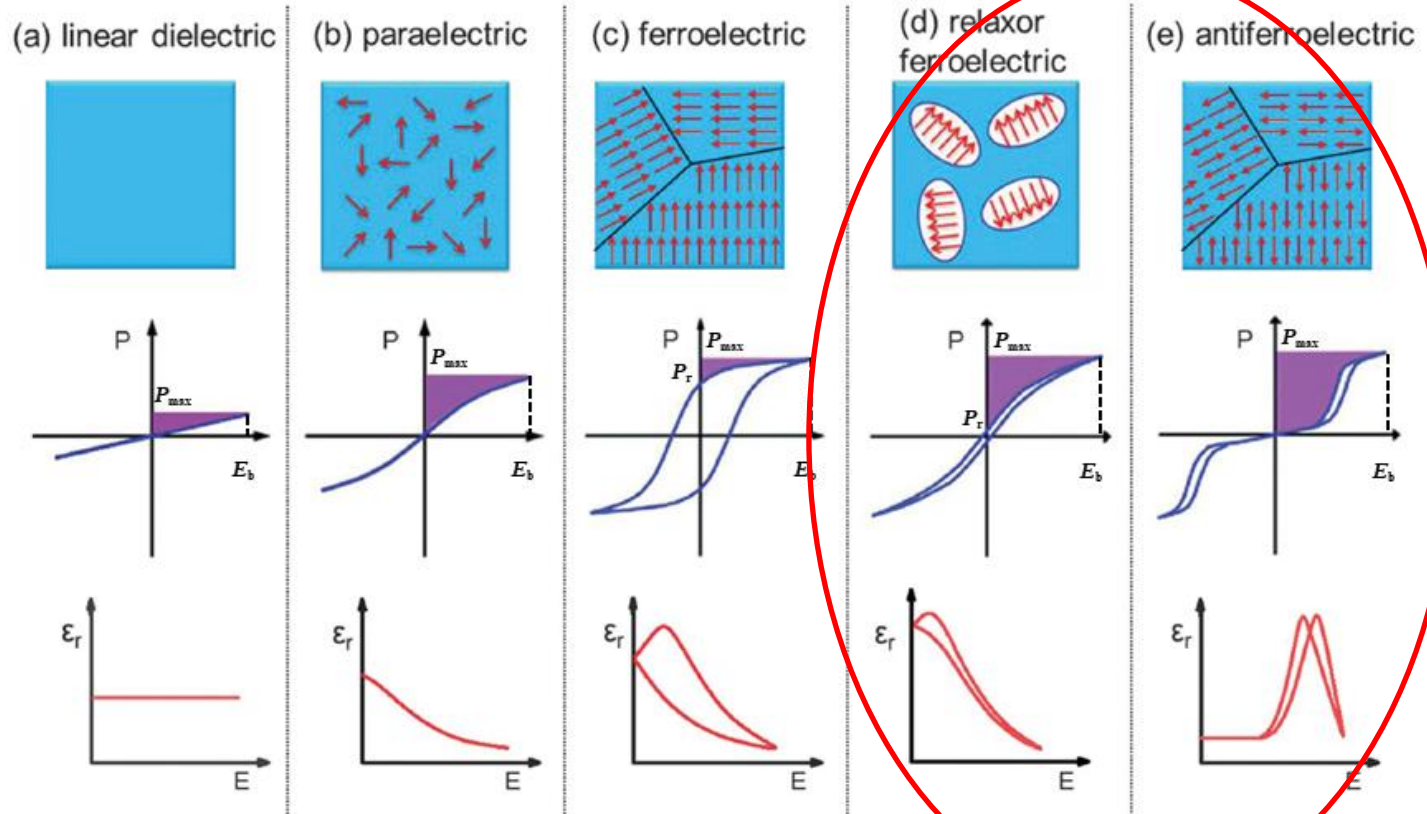
$$U_{\text{rec}} = \int_{P_r}^{P_{\max}} E dP$$

$$\eta = U_{\text{rec}}/U$$

$$U_{\text{loss}} = (U - U_{\text{rec}})$$

Energy storage in different materials

- Breakdown strength (E_b) means the maximum electric field that the material can withstand.

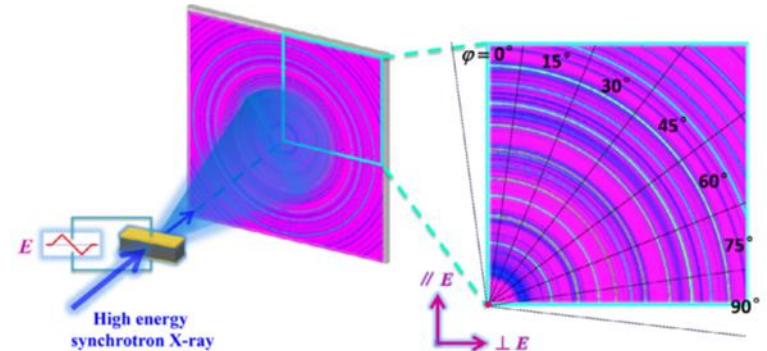


Develop lead-free electroceramics for high energy density capacitors

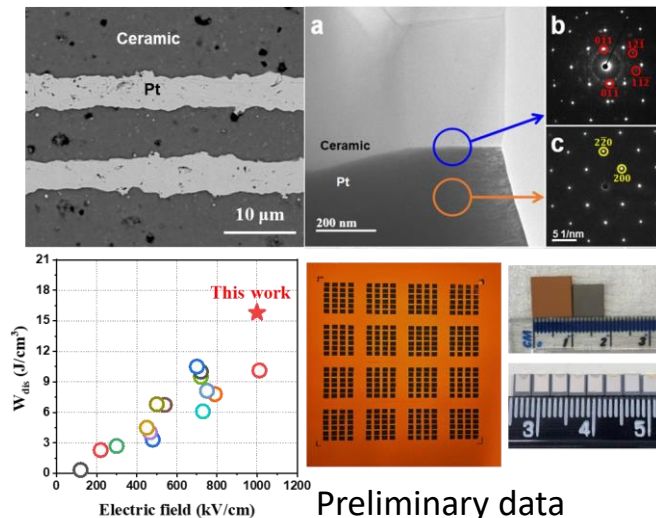
Step 1: Design novel material compositions by defect chemistry tailoring

- Vacancy design
- Element doping
- New endmember alloying

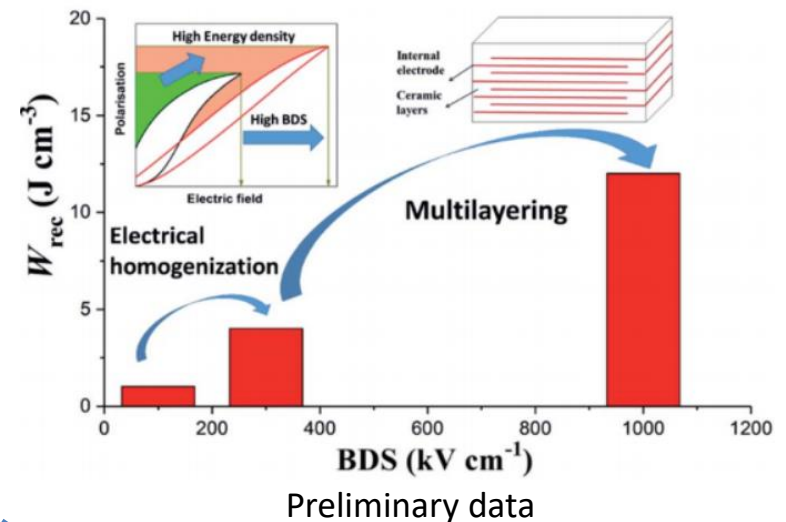
Step 2: Clarify the influence of defect chemistry



Step 3: Optimise the energy density

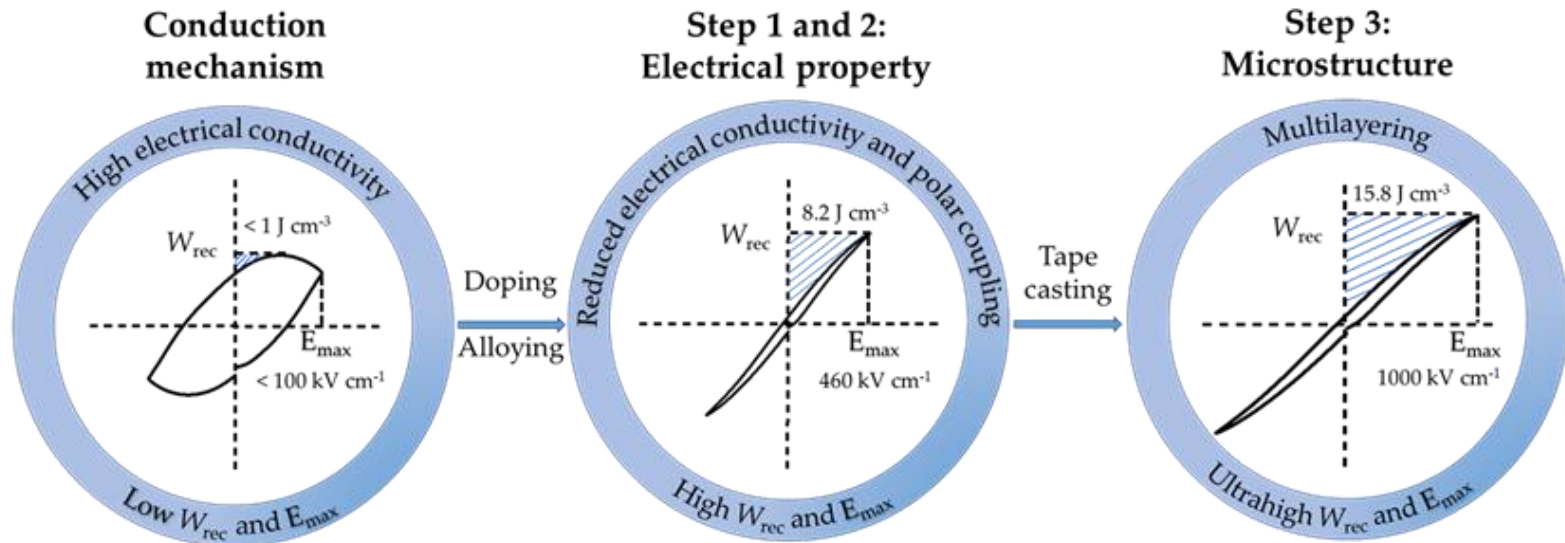


Step 4: Propose systematic strategies



Systematic strategy

Develop a systematic strategy



Schematic representation of the approach to obtain high energy density

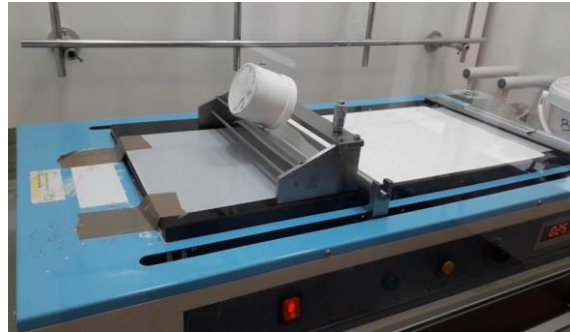
$$W = \frac{1}{2} QV = \frac{1}{2} CV^2 = \frac{1}{2} \epsilon_0 \epsilon_r \frac{A}{d} V^2 \quad A \uparrow \quad \epsilon_r \uparrow \quad d \downarrow \quad V \uparrow \quad \longrightarrow \quad W \uparrow$$

Multilayer Ceramic Capacitors (MLCCs) Manufacture

Planetary Ball Mill



Tape Casting



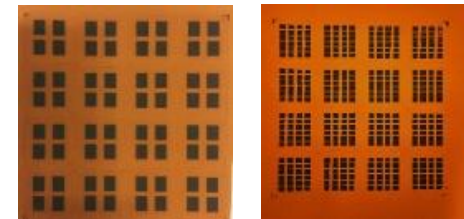
Screen Printing



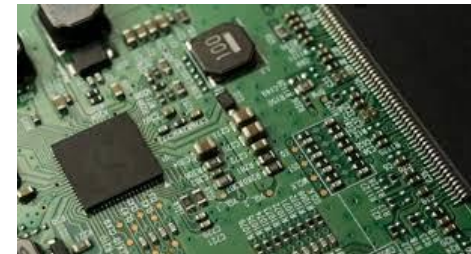
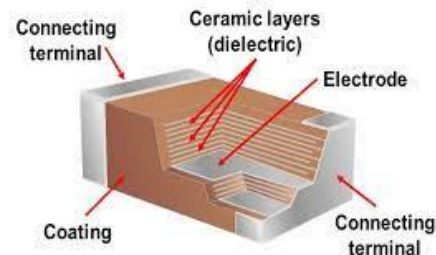
Hot Pressing



Samples

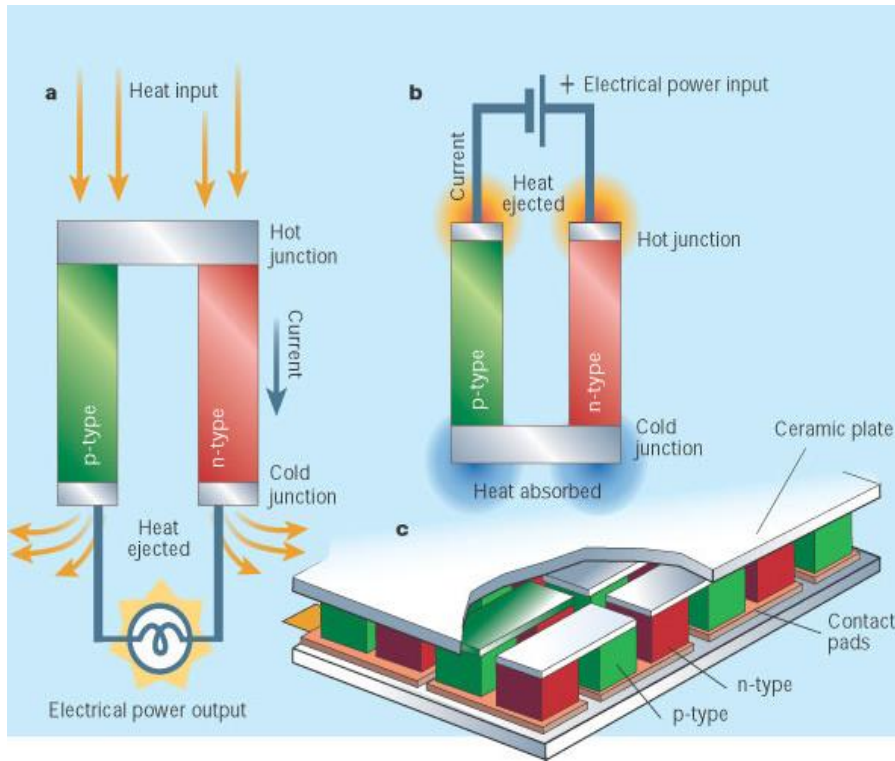


Multilayer Ceramic Capacitors (MLCCs)



Thermoelectric oxides for energy conversion and harvesting

Thermoelectric Generator



Thermoelectric materials can convert heat into electricity directly, vice versa.

Advantages:

- No moving parts
- Little to no maintenance
- Silent operation
- Same system for heating/cooling
- Size

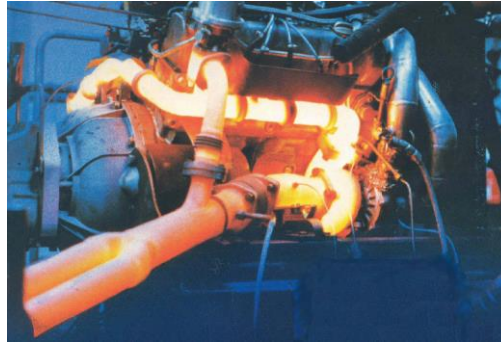
Disadvantages:

- Lower efficiency
- High cost

Applications



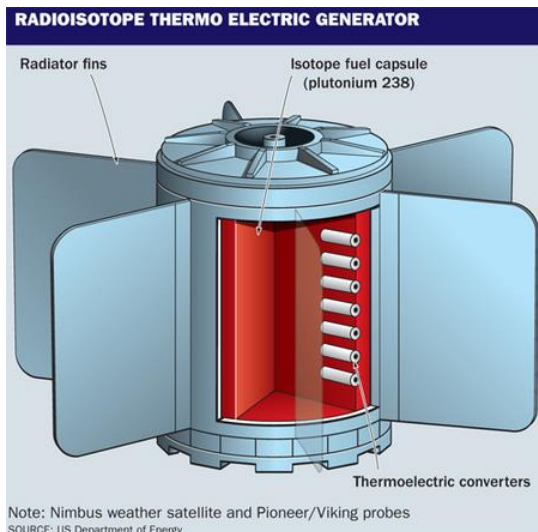
Thermoelectric
Wristwatch



Thermoelectric power generation



Thermoelectric IR
detectors



Multiple Mission Radioisotope
Thermoelectric Generator



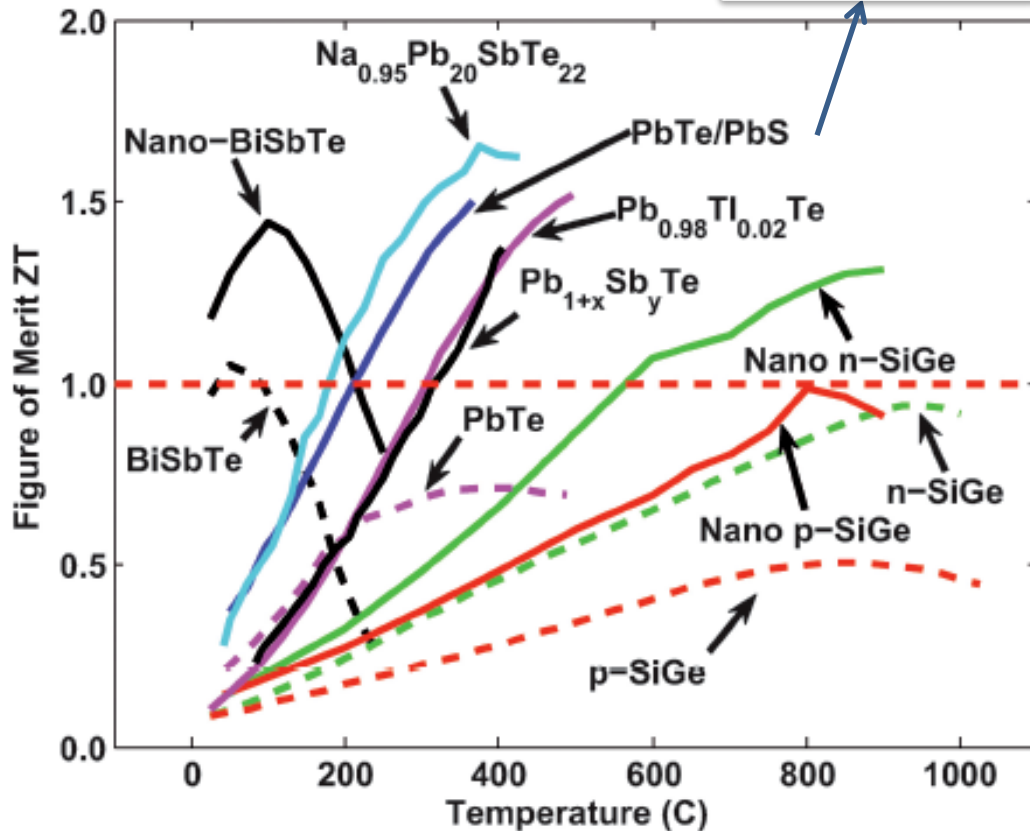
Thermocouples



Thermoelectric mini-refrigerators

Thermoelectric figure of merit

toxic, rare



- ZT=1 is regarded as a performance benchmark for viable TE materials.

- Figure of merit is given by:

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

- For a high ZT, usually electrical conductivity lies between 100 S/cm and 1000 S/cm.

The strategies for improving thermoelectric performance

❑ Increasing power factor ($S^2 \sigma$)

- A balance must be found between effective mass and mobility for a high power factor.

❑ Lowering thermal conductivity (κ)

- Introduce point defects or vacancies. (SrTiO₃ based system)
- Engineer complex crystal structures to separate the electron-crystal from the phonon-glass.
- Create nanostructures thus shortening the mean free path. These materials can be formed as superlattices (2D structures), nanowires (1D structures), quantum dots (0D structures) and thin-film materials.

Nominal doping mechanisms

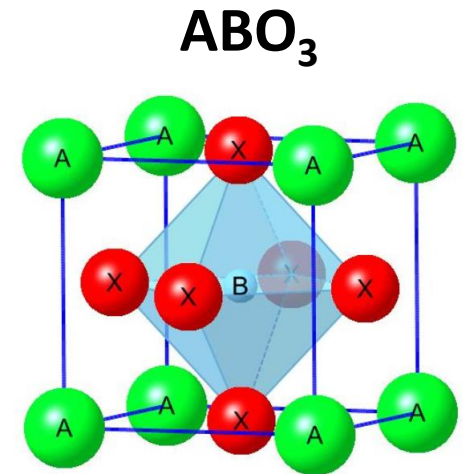
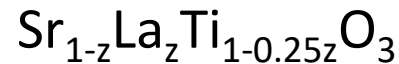
Electronic compensation (e): $\text{Sr}_{\text{Sr}}^x \rightarrow \text{La}_{\text{Sr}}^\bullet + e'$,



A-site vacancy (V_a): $3\text{Sr}_{\text{Sr}}^x \rightarrow 2\text{La}_{\text{Sr}}^\bullet + V_{\text{Sr}}''$

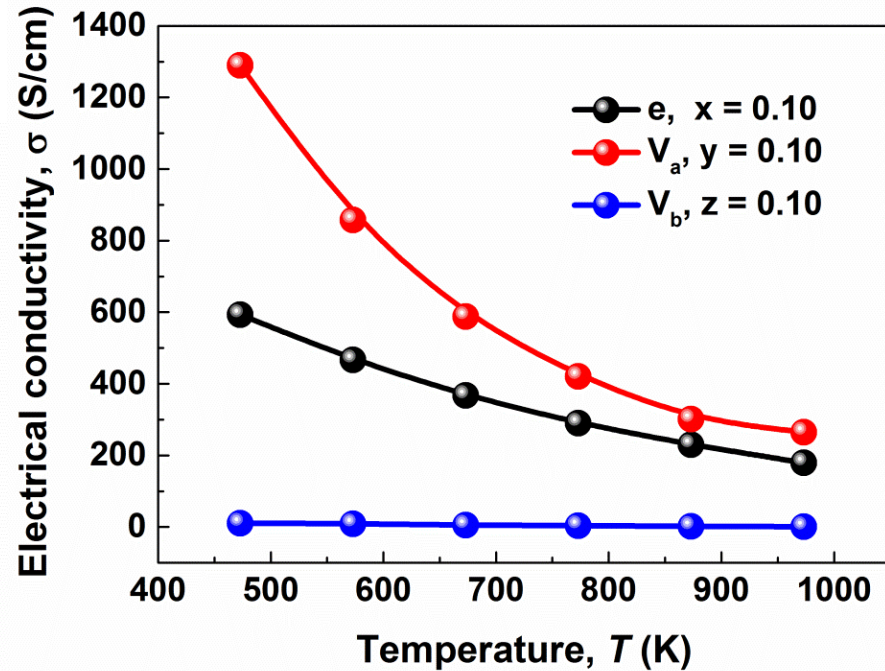
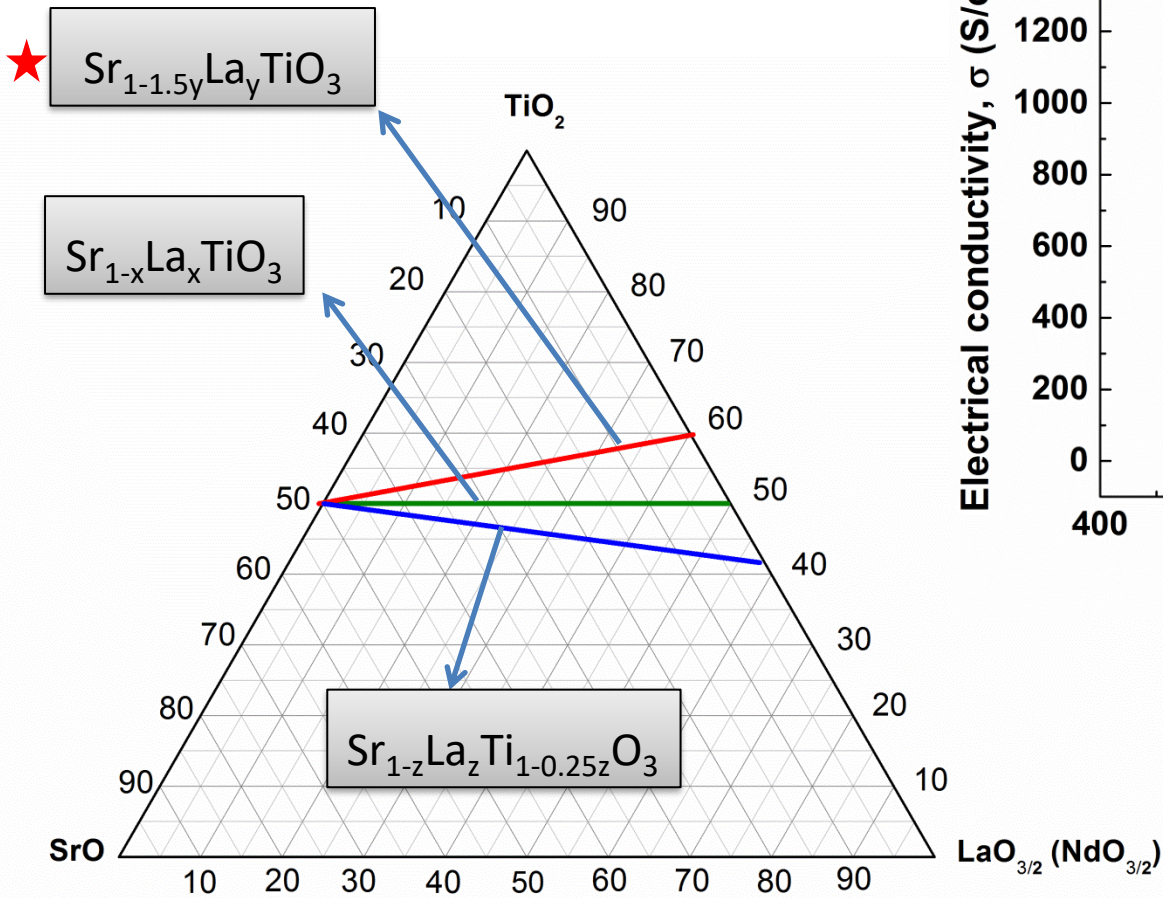


B-site vacancy (V_b): $4\text{Sr}_{\text{Sr}}^x + \text{Ti}_{\text{Ti}}^x \rightarrow 4\text{La}_{\text{Sr}}^\bullet + V_{\text{Ti}}''''$



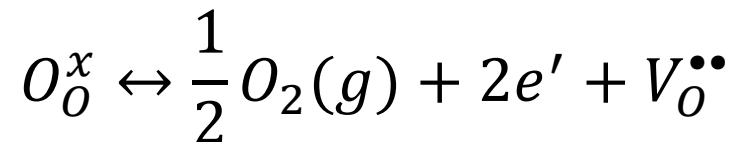
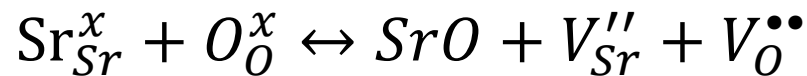
Aim: To introduce A-site/B-site/O vacancy to improve the thermoelectric performance by reducing thermal conductivity without decreasing the electrical conductivity.

La doped SrTiO₃ - N₂/5%H₂



A-site (Sr) vacancy is beneficial for the improvement of electrical conductivity as compared to stoichiometric compounds.

Why A-site vacancy is beneficial for the improvement of electrical conductivity?



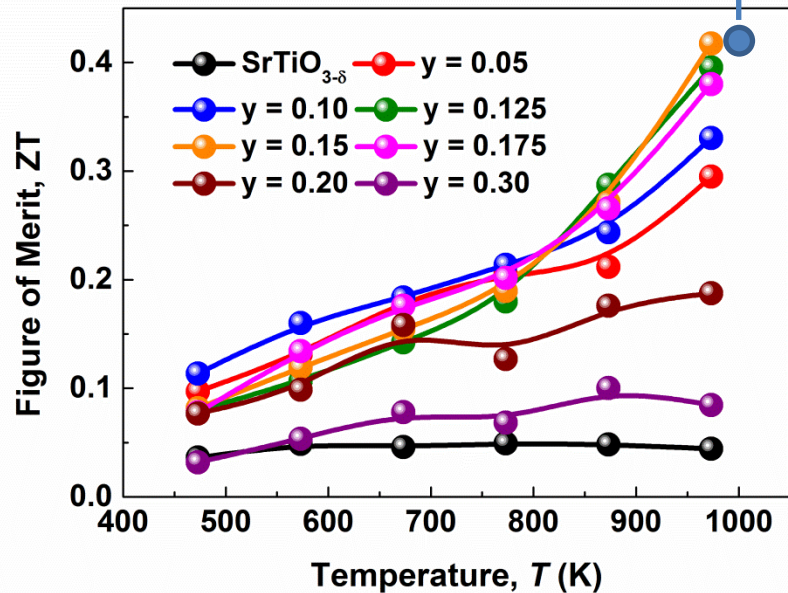
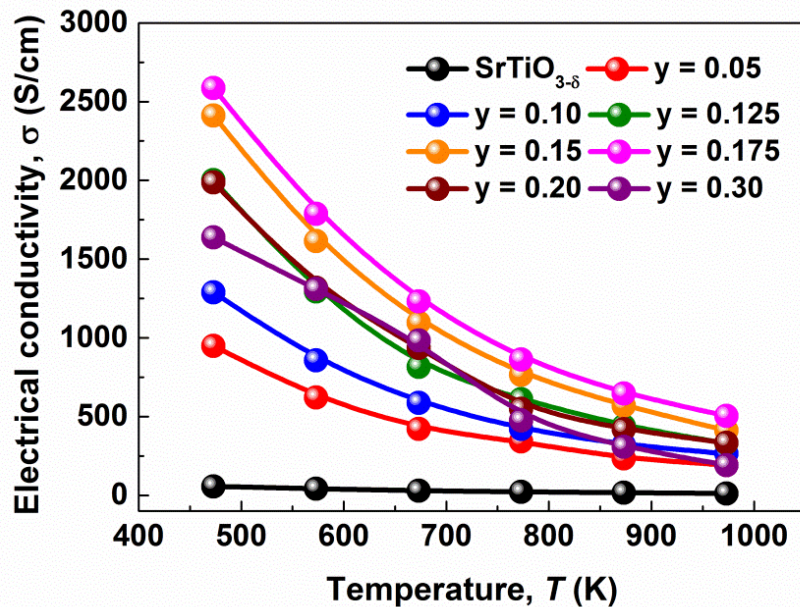
V_{Sr}'' reduces the number of intrinsic Schottky defects, pushing the first equation to the left and thus reducing $V_{\text{O}}^{\bullet\bullet}$. For a given $p\text{O}_2$, the second equation shifts right to oppose the change, facilitating oxygen removal from the lattice associated with the generation of free electrons.^[5]

[5] D. Neagu and J. T. S. Irvine. *Chemistry of Materials*, 23, 1607–1617 (2011).

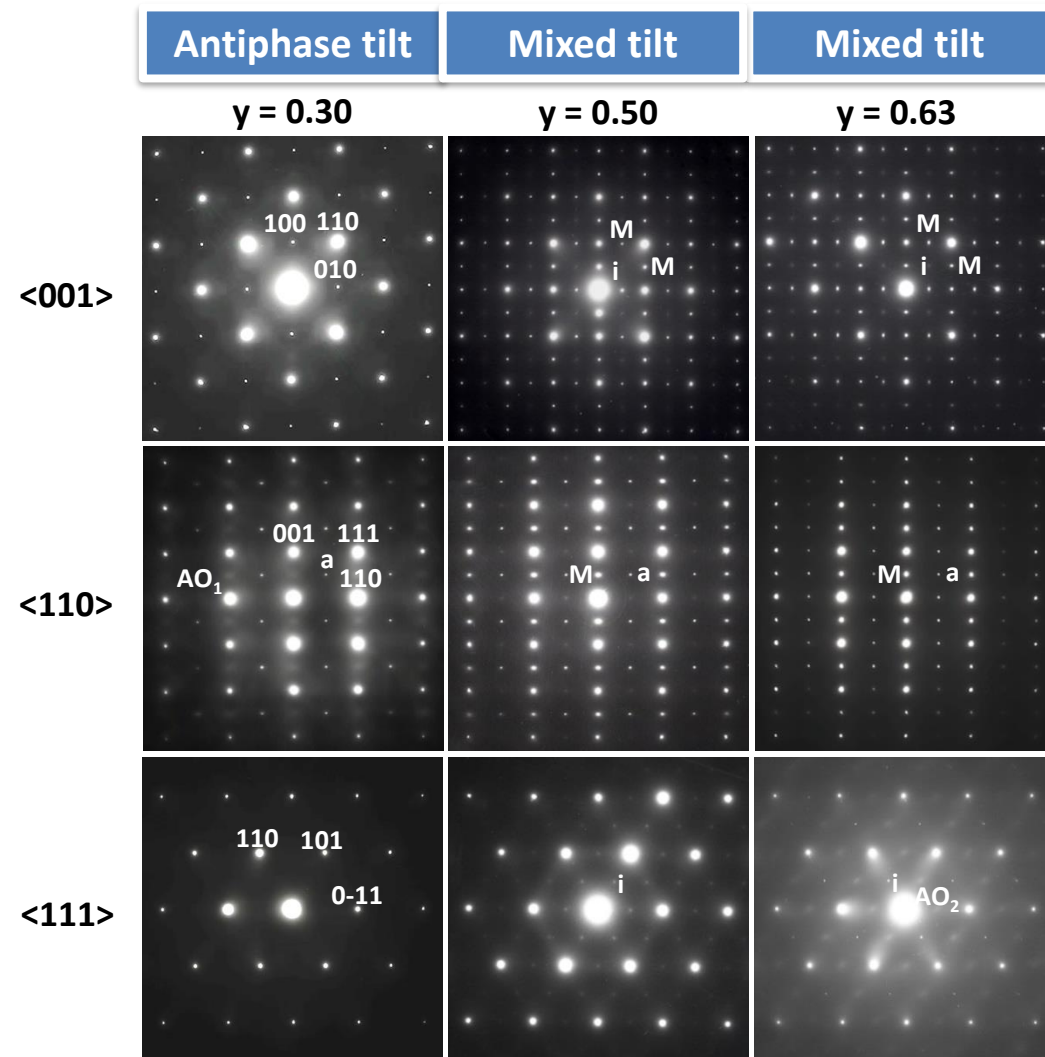
Thermoelectric properties of La doped SrTiO₃

Highest ZT values reported for n-type ST based ceramics and exceeds the current record for an n-type material based on epitaxial thin films.

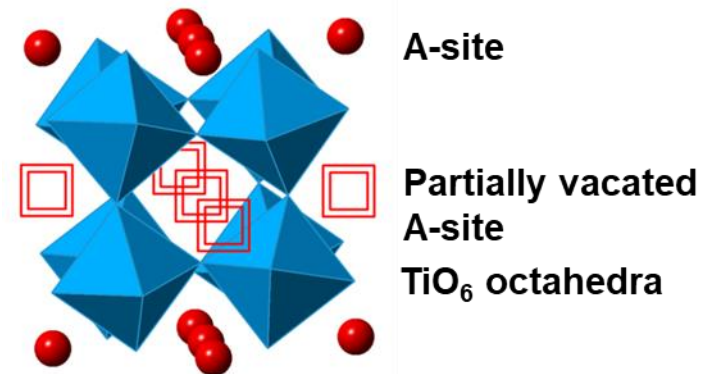
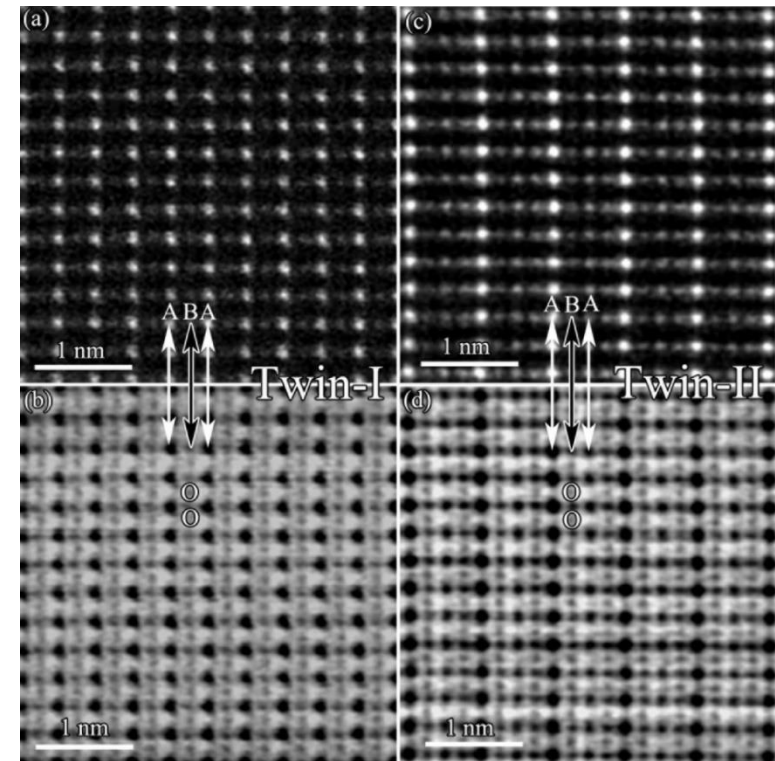
Highest ZT value reported in 20% Nb doped SrTiO₃ epitaxial film in 2005^[6].



Atomic microstructure

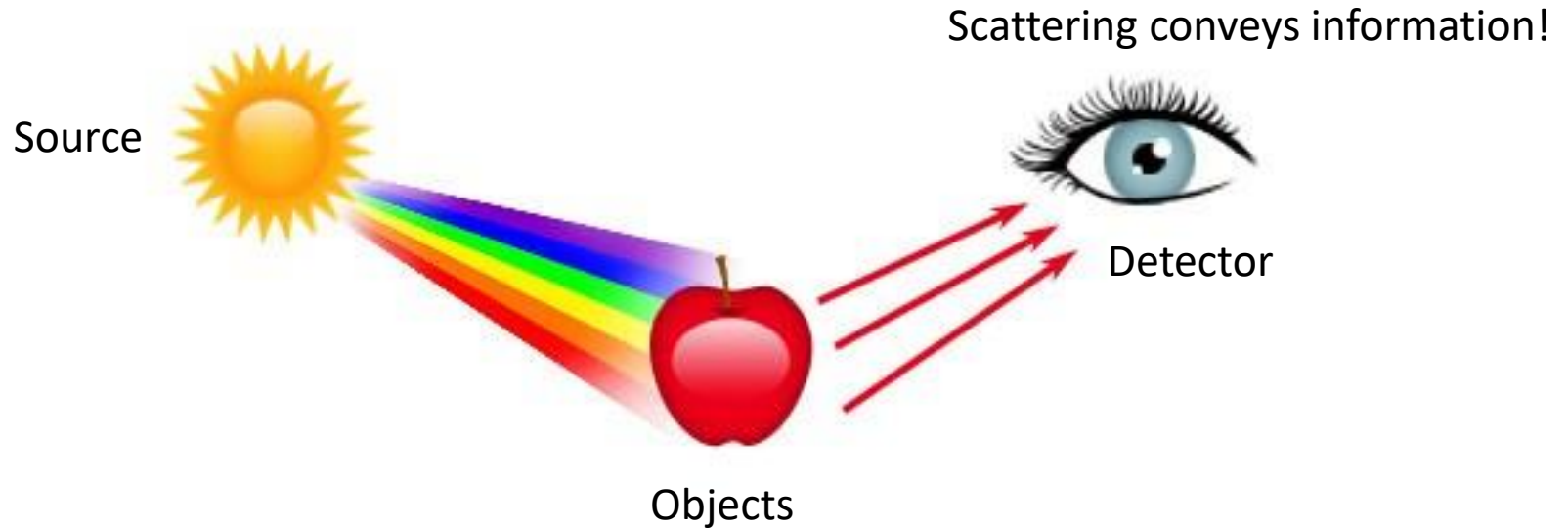


Atomic resolution HAADF-STEM images



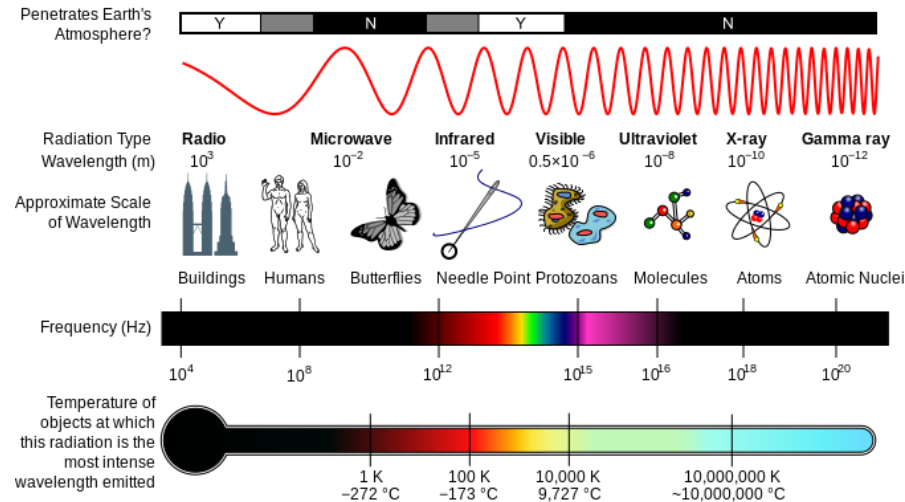
Advanced characterization technique-neutron scattering

Why can we see?



1. We can see something when light scatters from them.
2. Visible light is composed of electromagnetic waves, thus we are using electromagnetic probe to observe objects.
3. However, the details of what we see are ultimately limited by the wavelength.

How can we see atomic scale?



A diagram of the electromagnetic spectrum, showing various properties across the range of frequencies and wavelengths

- To “see” atomic structure, we require a probe with a wavelength at length scale of interest, such as $\sim 10^{-10}$ m.

- | | |
|--------------|---|
| 1. X-ray | A form of electromagnetic radiation ($\lambda \sim 10^{-8} - 10^{-10}$) |
| 2. Electrons | Charged particle ($\lambda = h/mv$) |
| 3. Neutron | Neutral particle ($\lambda = h/mv$) |

What is the advantages and disadvantages of neutron scattering?

Advantages

Wavelength are easily to be varied and comparable with interatomic spacings

Zero charged, extremely penetrating though atoms and not strongly attenuated

Nuclear interaction is simple only with nuclei of atoms and is easy to model

Non-destructive probe with low energy

Isotopic sensitivity and can see low elements easily, such as H

Magnetic dipole moment for study of magnetic materials

Disadvantages

Neutrons are expensive to produce

Neutron scattering experiments are time consuming and require international facilities

Interact weakly with matter means large samples are required

To “See” materials using neutron scattering

Structure and Dynamics

Elastic scattering (NS)

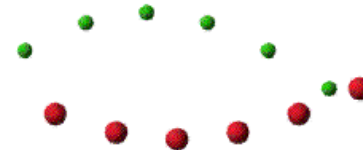
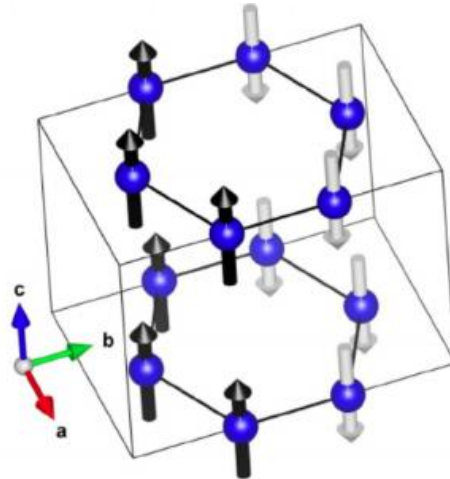
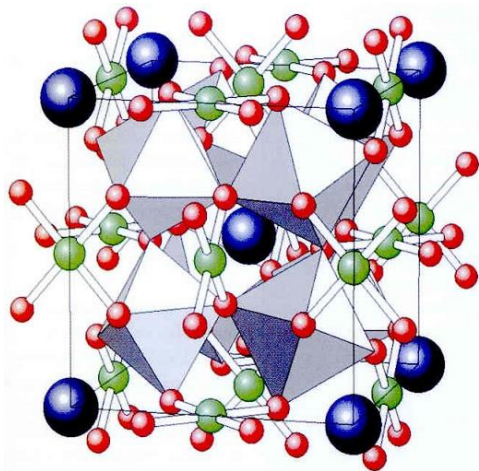
Inelastic scattering (INS)

Material structure

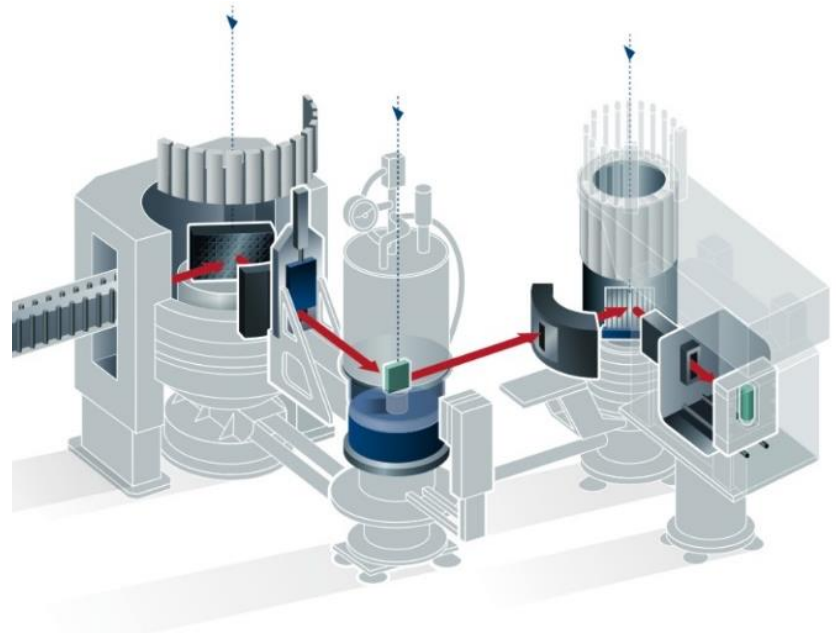
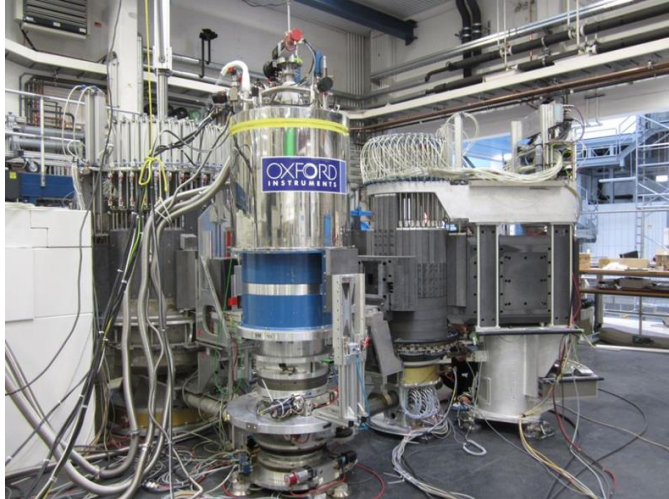
Magnetic structure

Phonon

Spin waves



FLEXX—the neutron triple-axis spectrometer



FLEXX is a **world-leading** instrument for inelastic neutron scattering at HZB:

- **Quantum magnetism**
- **Unconventional superconductivity**
- **Thermoelectric materials**

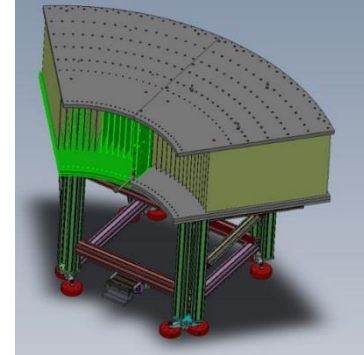
The versatility of FLEXX

- World leading sample environments allow access to a large parameter space for temperature and magnetic field.
- A novel multi-analyzer MultiFLEXX can measure many angles and multiple energy transfers simultaneously.
- High-resolution Neutron Resonance Spin Echo option.

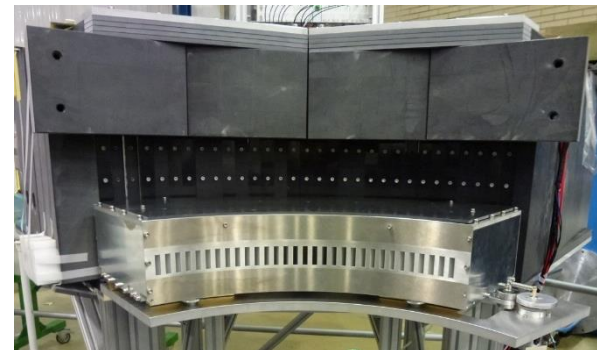
Extreme Sample Environments



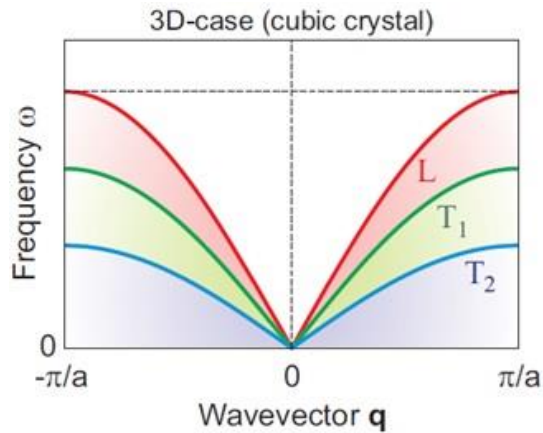
MultiFLEXX



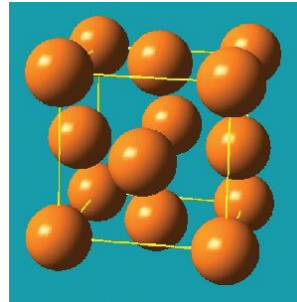
High-resolution Neutron Resonance Spin Echo



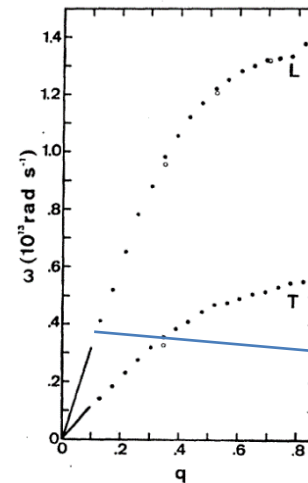
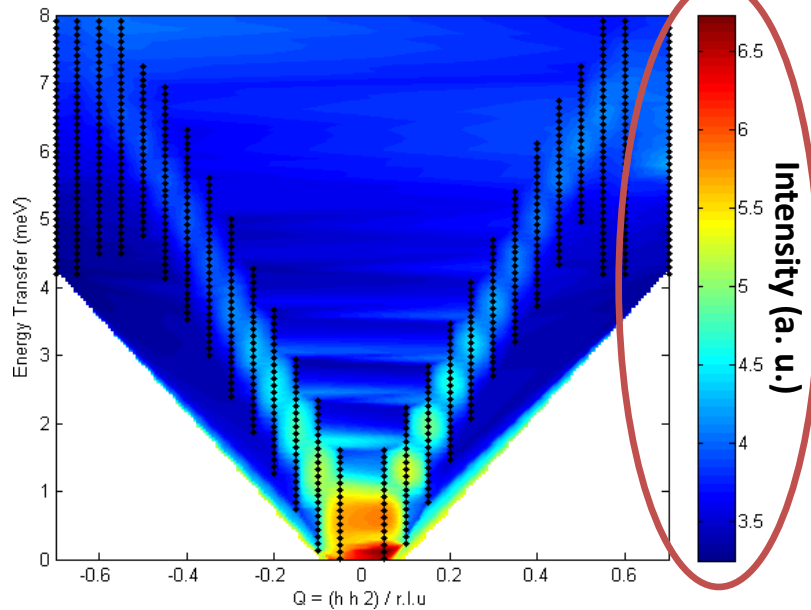
Example 1 – Lead phonon excitations



fcc nuclear structure



Pb –Lead Single Crystal

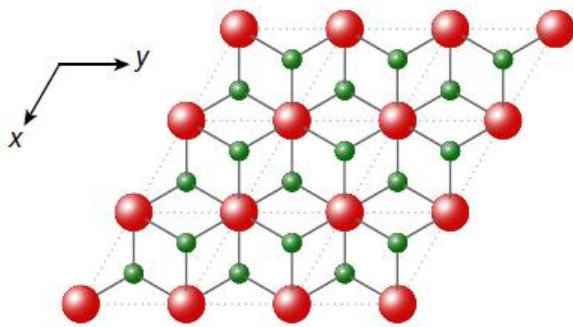


[8] Stedman, et al.,
Phys. Rev. 1967, **162**, 545.

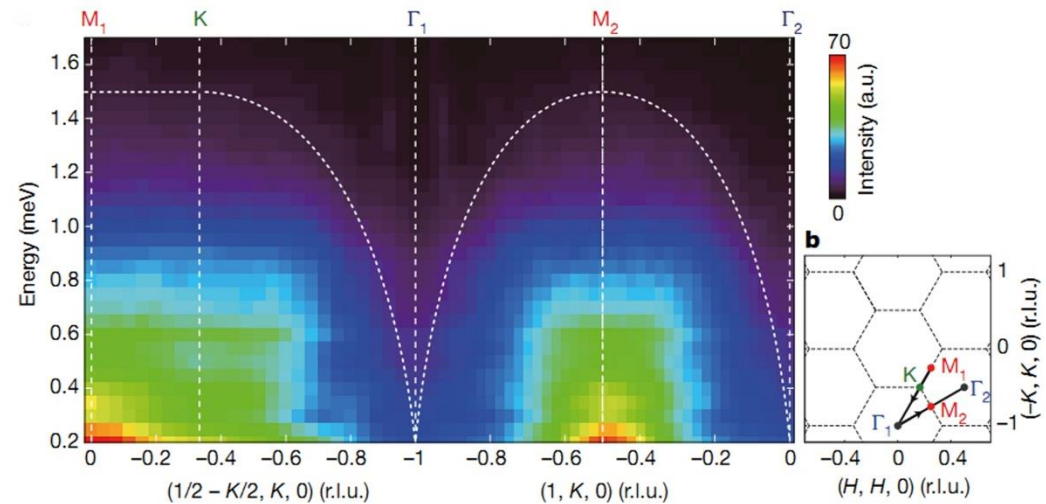
Extract the
velocity of sound

Example 2 – Quantum-Spin-Liquid (QSL)

The **broad continuum** of YbMgGaO_4 is an immediate consequence and strong evidence of spinon excitations in QSLs^[1].



A triangular layer of the magnetic Yb^{3+} ions and oxygen



A contour plot of the spin-excitation spectrum along the high symmetry momentum directions