

Spontaneous Electrical Polarization in Different Phases of Perovskite NaNbO_3

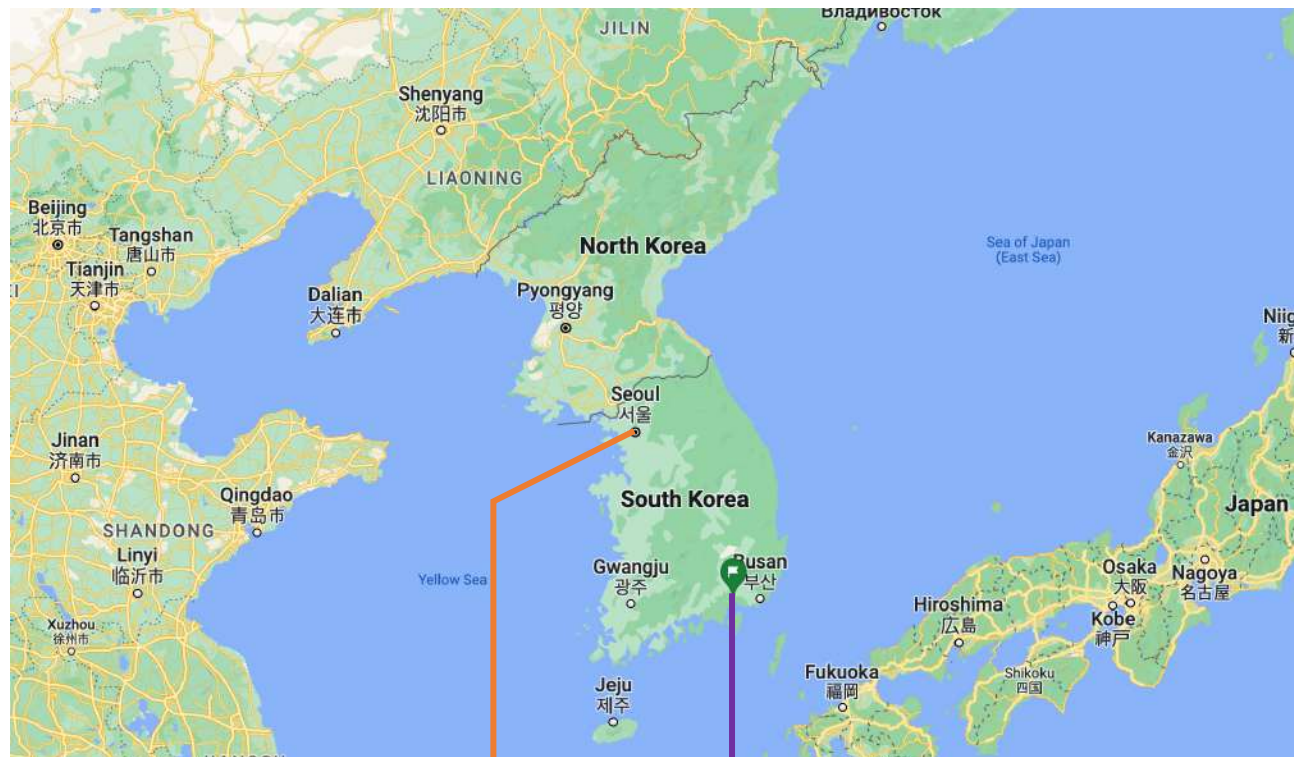
Kisung Kang

The NOMAD Laboratory at the FHI of the Max-Planck-Gesellschaft
and IRIS-Adlershof of the Humboldt-Universität zu Berlin





My Background



Seoul (서울)



Changwon (창원)

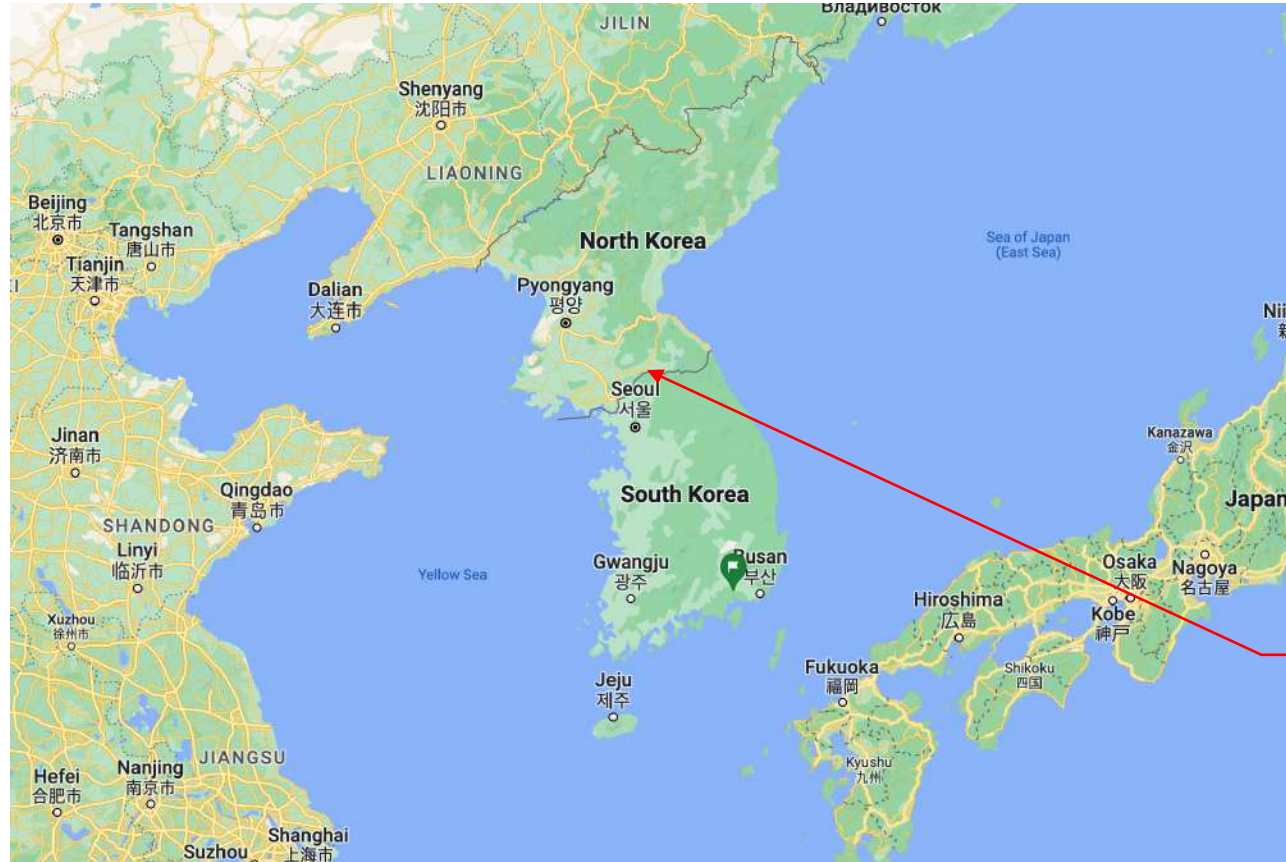
| Foods



| Culture



My Background



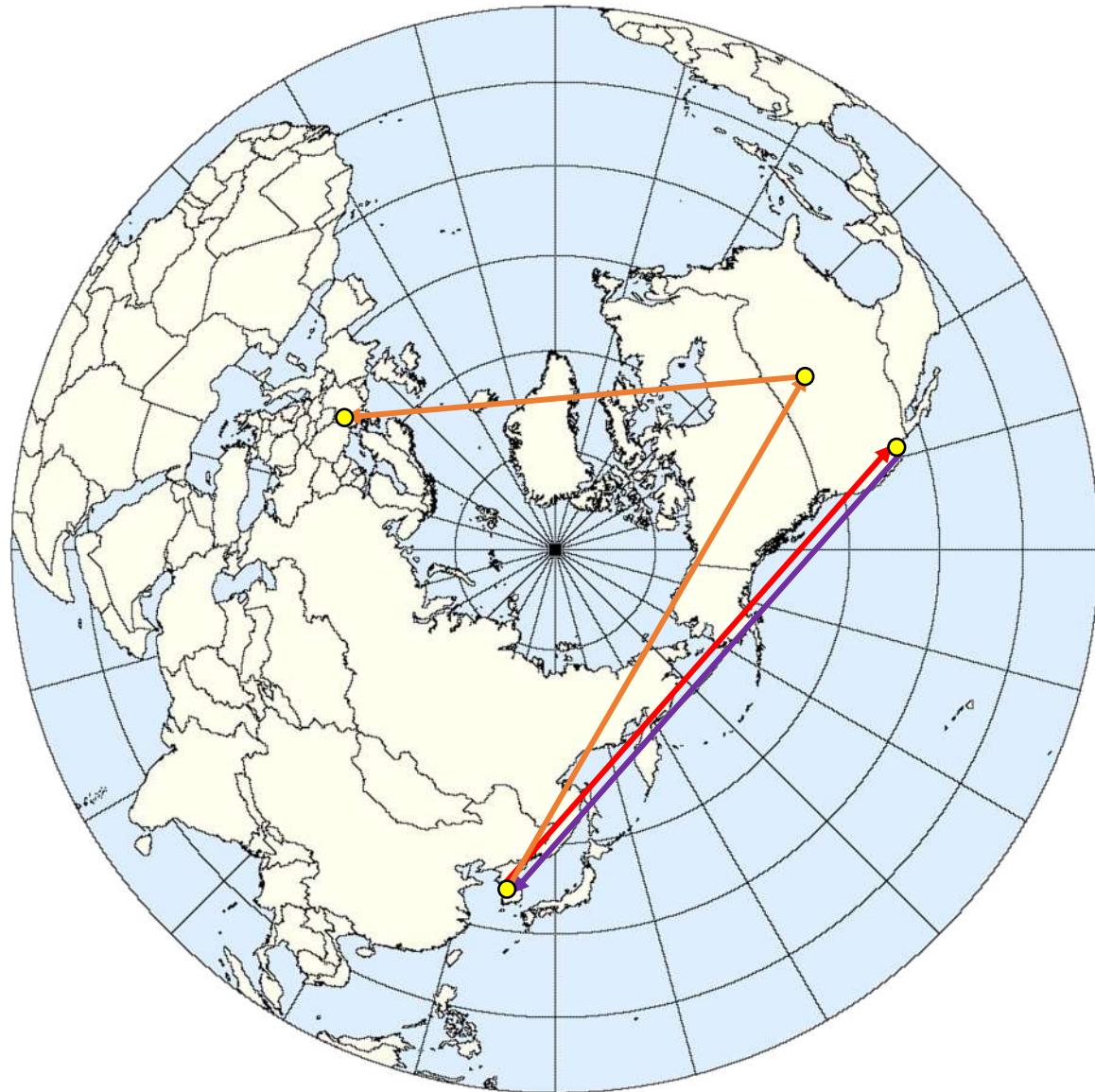
Scenery



Korean War (1950 -)

The war is officially paused not ended.
Thus, we are technically still at war.

My Background



| Undergraduate

Yonsei University

Electronic structure of phosphorene



Prof.
Aloysius
Soon

| Exchange program

University of California, Irvine

| PhD program

University of Illinois, Urbana-Champaign

Ground and excited state properties of antiferromagnetic metals



Prof.
André
Schleife



Prof.
David
Cahill

| Postdoc

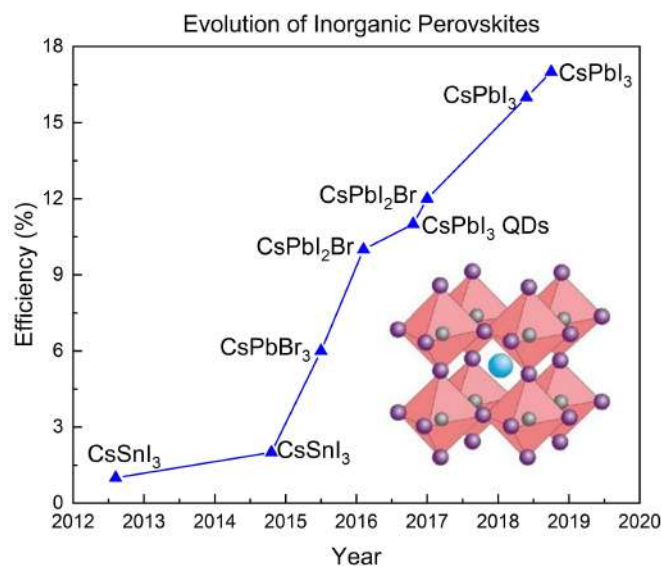
Fritz-Haber-Institut



NaNbO₃ is regarded as a promising lead-free perovskite

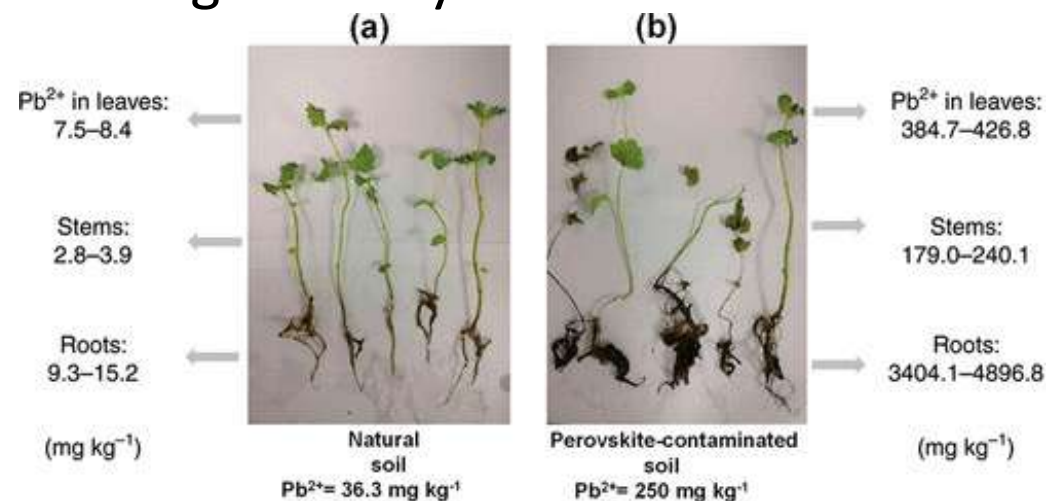
| Why lead-included perovskites (APbX₃)?

- Easy synthesis
- Cost-effective techniques
- High efficiency
 - Small carrier effective masses
 - High optical absorption coefficient
 - Excellent defect tolerance
 - High electronic dimensionality



| Then, Why not?

- Long-term instability
- High toxicity



| Then, Why NaNbO₃?

- Piezo/ferroelectric properties
- Many different phases
- Strain engineering

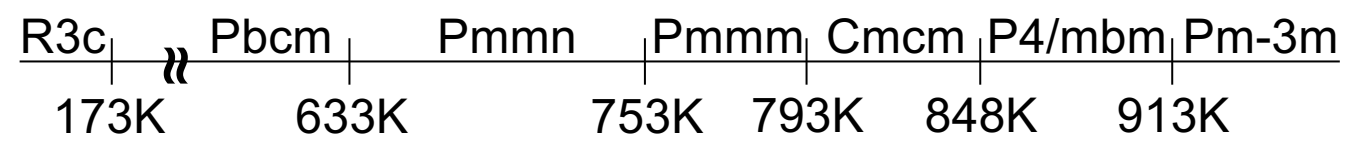
Diversity can be a complicate problem

[1] M. Wang *et al.* *Nano-Micro Lett.* **13**, 62 (2021) [3] V. K. Ravi *et al.* *ACS Omega* **5**, 46 (2020)
 [2] Q. Tai *et al.* *Energy Environ. Sci.* **12**, 2375 (2019) [4] J. Schwarzkopf *et al.* *J. Appl. Cryst.* **45**, 1015 (2012)

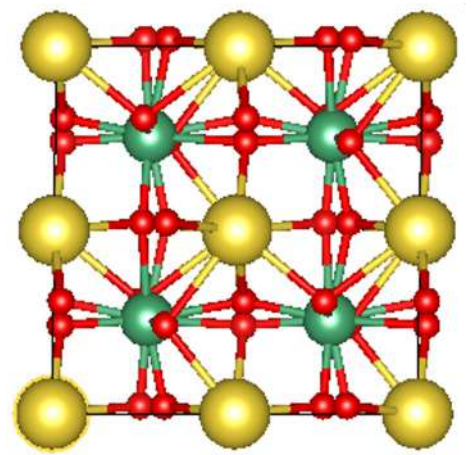
Various phases of Bulk NaNbO_3 appear at normal pressure



Phase diagram of bulk perovskite NaNbO_3

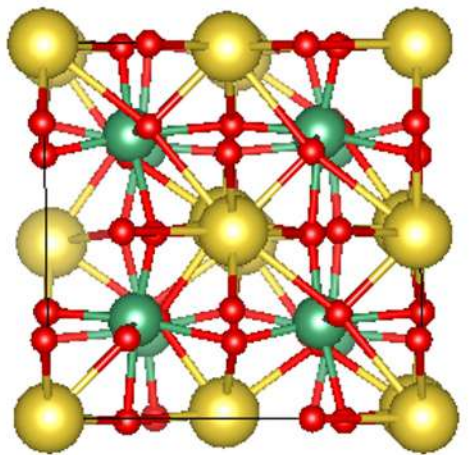


R3c



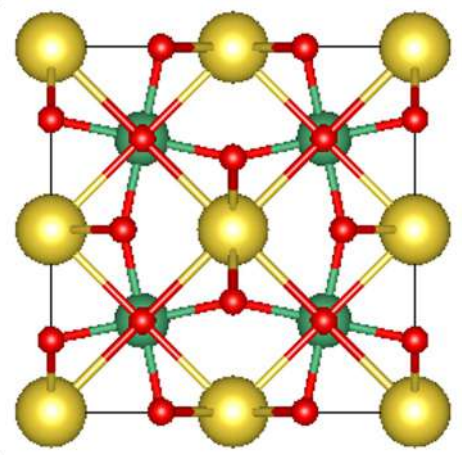
$$P = [0.3, 0.3, 0.3]$$

Pbcm



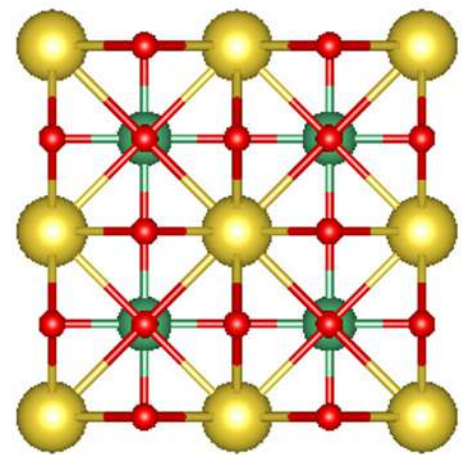
$$P = [0.0, 0.0, 0.0]$$

P4mbm



$$P = [0.0, 0.0, 0.0]$$

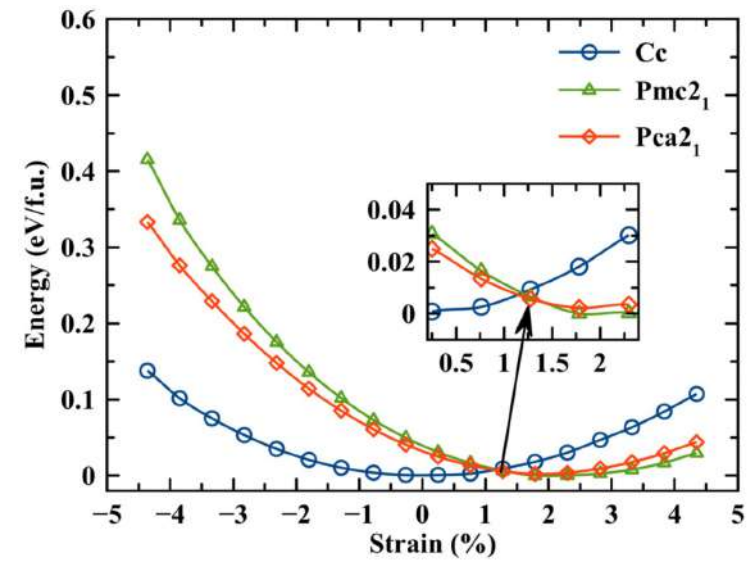
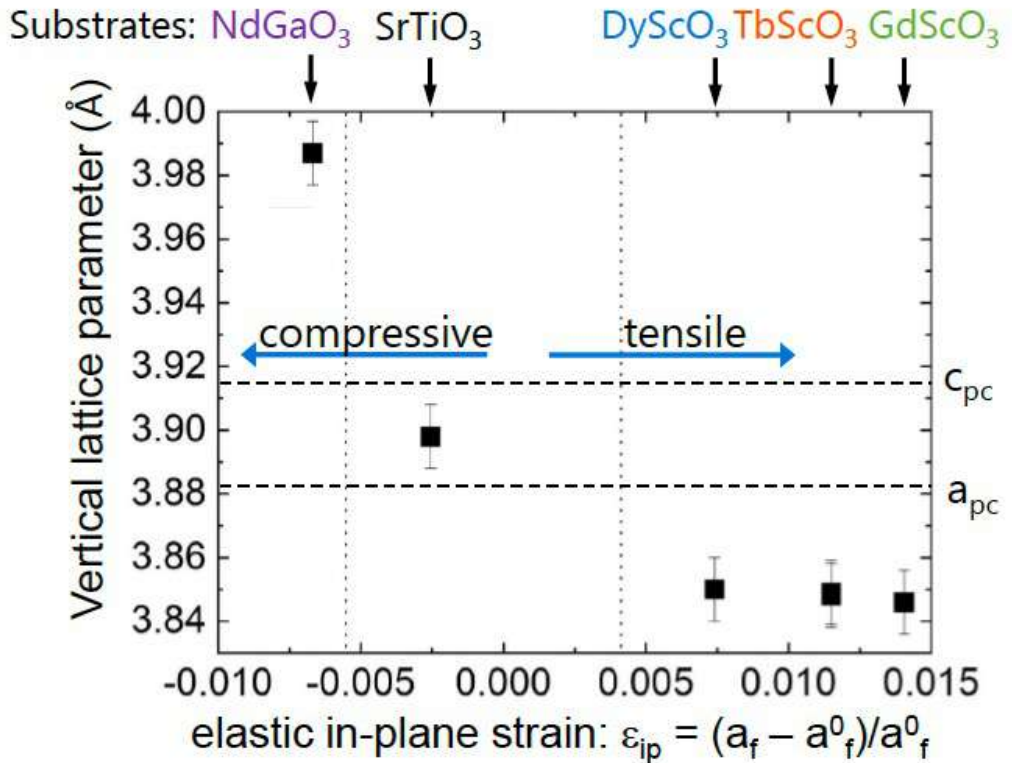
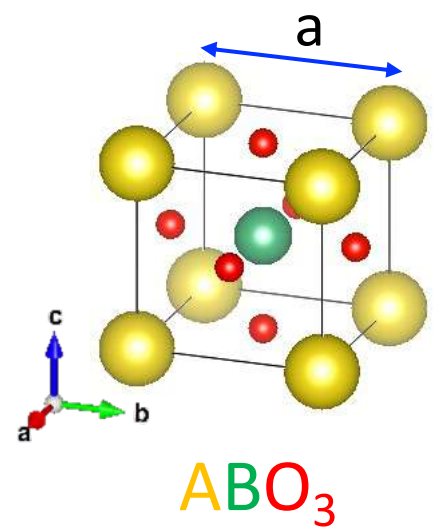
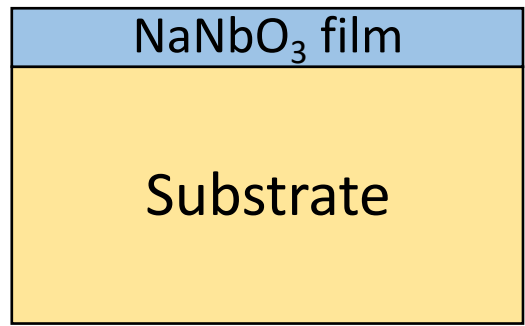
Pm-3m



$$P = [0.0, 0.0, 0.0]$$



NaNbO₃ thin films have more complicate phase diagram



How can we identify the phase of NaNbO₃ thin film which is different from bulk?

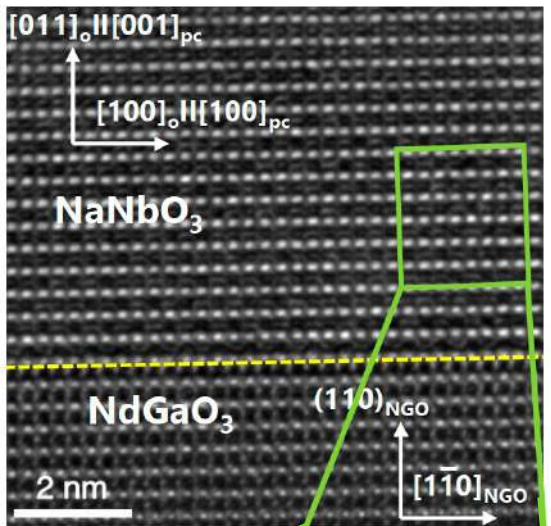
Symmetry and lattice structure? Electrical polarization? Band gap? Optical properties?

[1] K. Patel, et al., Phys. Rev. B 103, 094103 (2021)



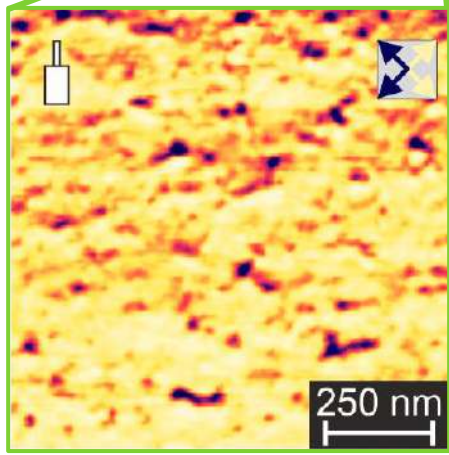
Phase of NaNbO_3 films might be identified by polarization

Compressive strain $|\text{NaNbO}_3/\text{NdGaO}_3$



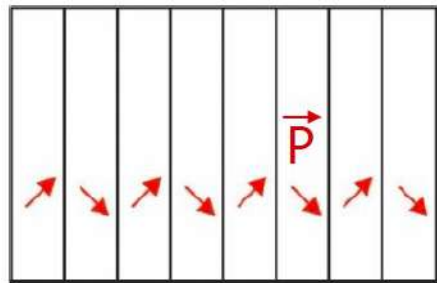
- Orthorhombic structure

a	3.861 Å
b	3.855 Å
c	3.94 Å



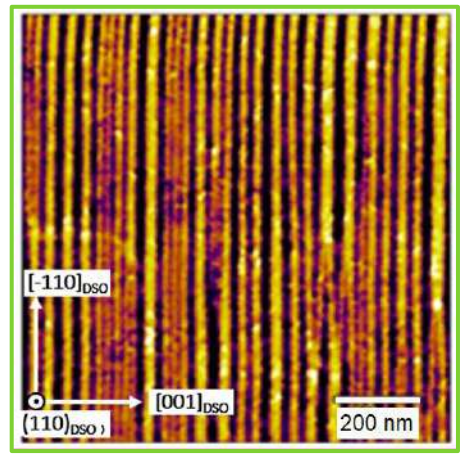
- Electrical polarization
- Out-of-plane direction
: [001]

Tensile strain $|\text{NaNbO}_3/\text{DyScO}_3$



- Monoclinic structure

a	3.87 Å
b	3.947 Å
c	3.952 Å

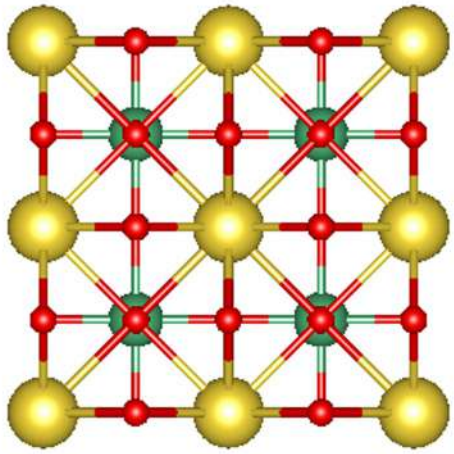


- Electrical polarization
- In-plane direction
[011]
- Band gap: $E_g = 3.9 \text{ eV}$

Investigation of Proposed Phases in the Perovskite NaNbO_3

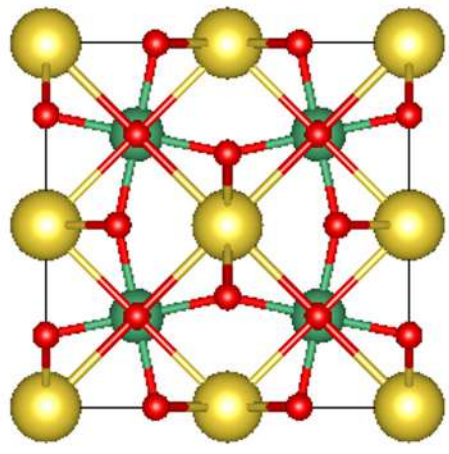


|Pm-3m



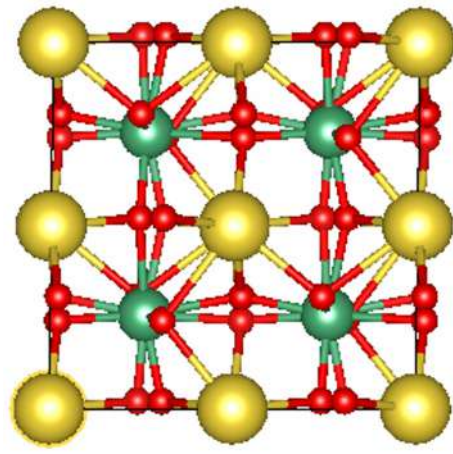
Cubic

|P4mbm



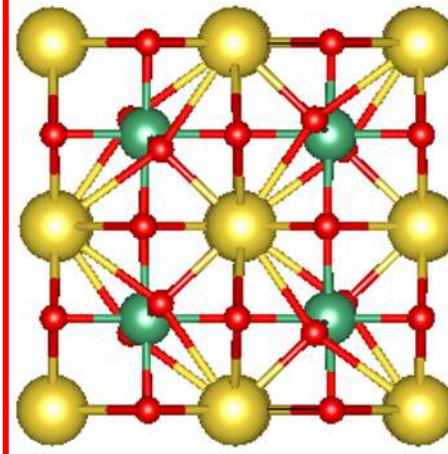
Tetragonal

|R3c

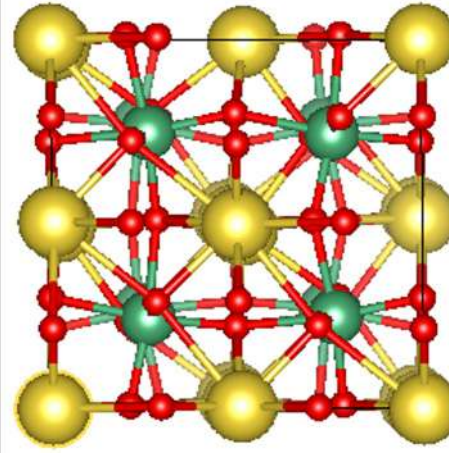


Trigonal

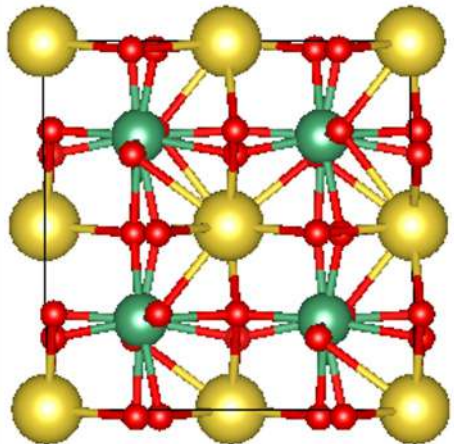
|Cmcm



|Pca2₁

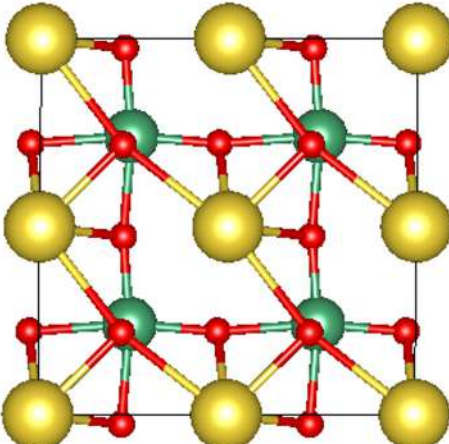


|Cc

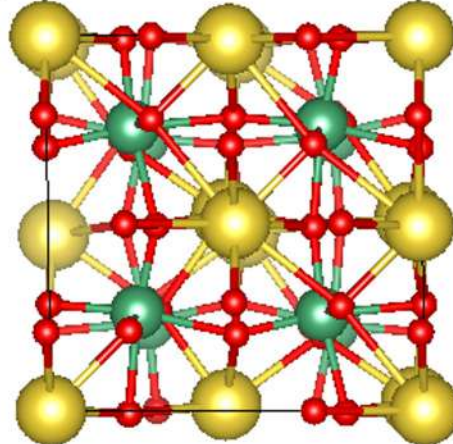


Monoclinic

|Pm

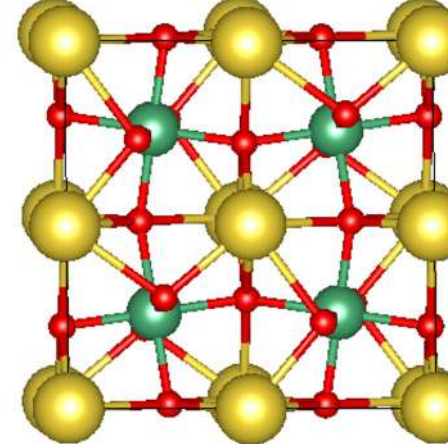


|Pbcm

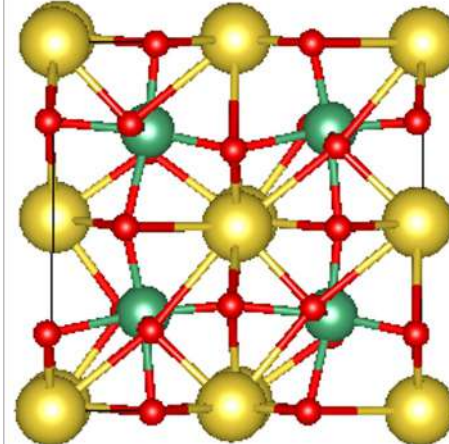


Orthorhombic

|Pnma



|Pmc2₁





Investigation of Proposed Phases

Tensile strain

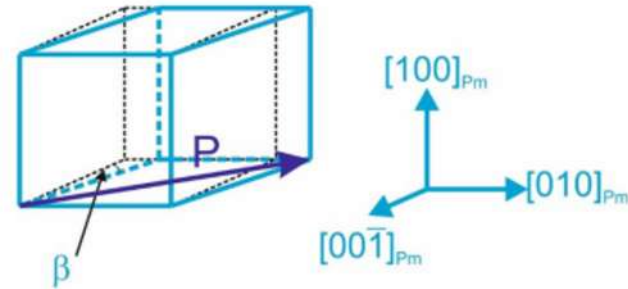
|NaNbO₃/DyScO₃

- Monoclinic structure
- Electrical polarization
- In-plane direction [011]

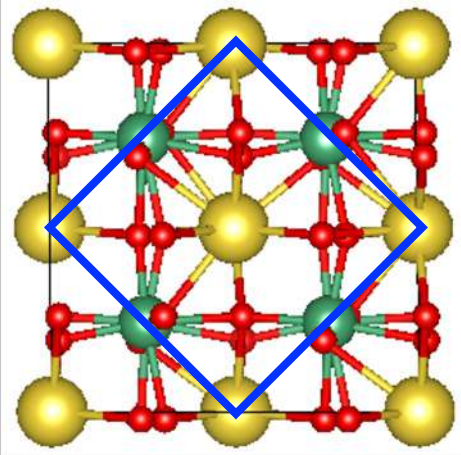
a	3.87 Å
b	3.947 Å
c	3.952 Å

α	89.5°
β	90°
γ	90°

- Band gap: $E_g = 3.9 eV$



|Cc



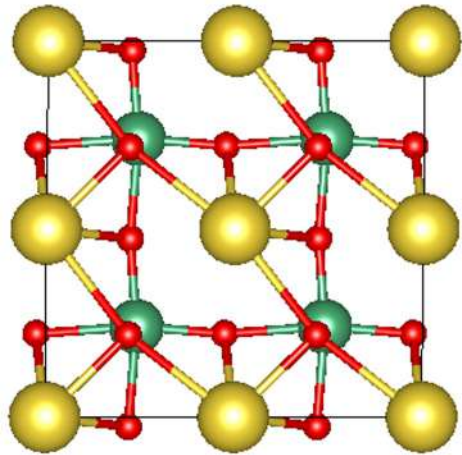
a	5.500 Å	-
b	5.572 Å	-
c	9.527 Å	-

α	90°	-
β	125°	-
γ	90°	-

$P = [0.3, 0.3, 0.3]$

$E_g(\text{HSE}) = 4.2 eV$

|Pm



a	3.934 Å	1.6%
b	3.947 Å	0.0%
c	3.952 Å	0.0%

α	89.4°	-0.1%
β	90°	0.0%
γ	90°	0.0%

$P = [0.0, 0.3, 0.3]$

$E_g(\text{HSE}) = 3.5 eV$



Investigation of Proposed Phases

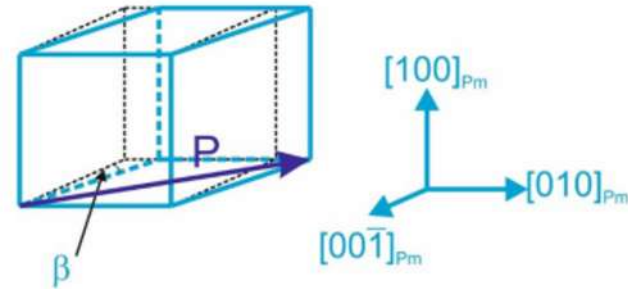
Tensile strain

$\text{NaNbO}_3/\text{DyScO}_3$

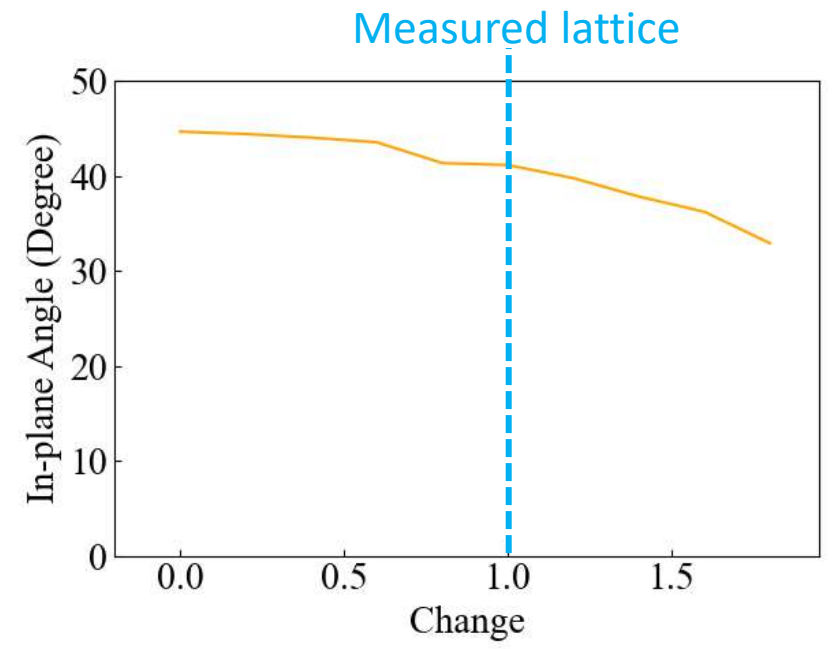
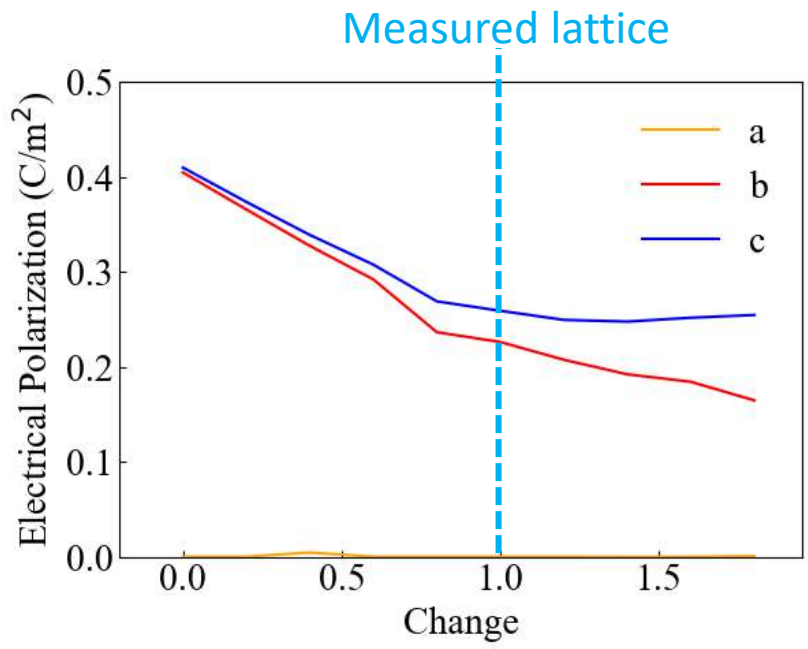
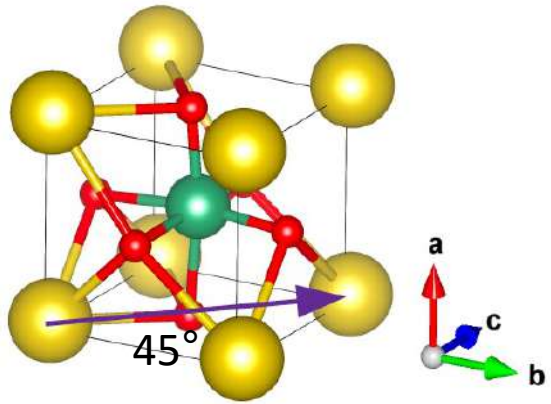
- Monoclinic structure
- Electrical polarization
- In-plane direction $[011]$

a	3.87 Å	α	89.5°
b	3.947 Å	β	90°
c	3.952 Å	γ	90°

• Band gap: $E_g = 3.9 \text{ eV}$



Pm





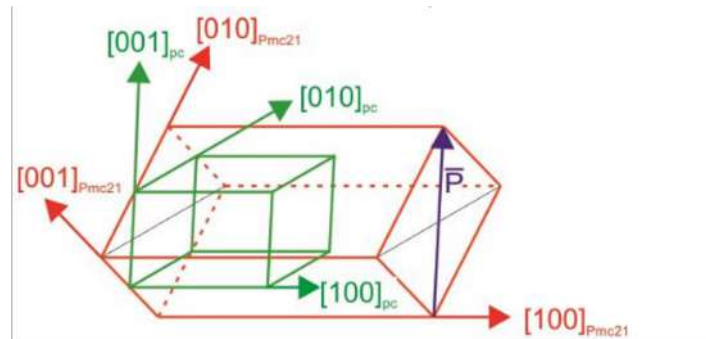
Investigation of Proposed Phases

Compressive strain

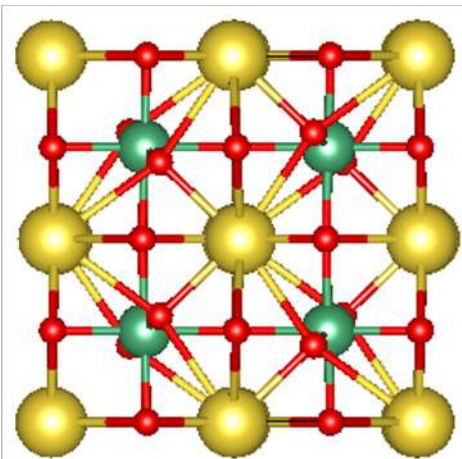
$\text{NaNbO}_3/\text{NdGaO}_3$

- Orthorhombic structure
- Electrical polarization
 - Out-of-plane direction $[001]$

a	3.861 Å
b	3.855 Å
c	3.94 Å



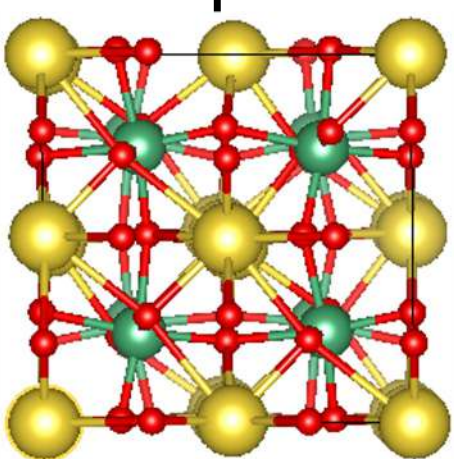
Cmcm



a	3.909 Å	1.2%
b	3.864 Å	0.2%
c	3.911 Å	-0.7%

$$P = [0.0, 0.0, 0.0]$$

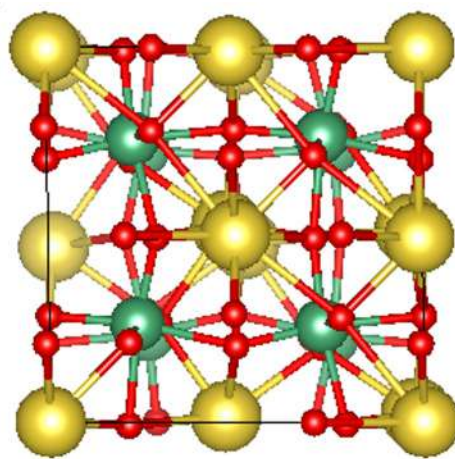
Pca2_1



a	3.961 Å	-1.3%
b	3.897 Å	-0.8%
c	3.978 Å	-1.7%

$$P = [0.0, 0.2, 0.0]$$

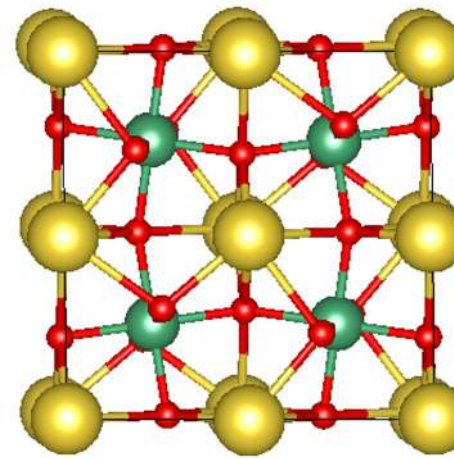
Pbcm



a	3.992 Å	-2.1%
b	3.805 Å	1.6%
c	4.030 Å	-3.0%

$$P = [0.0, 0.0, 0.0]$$

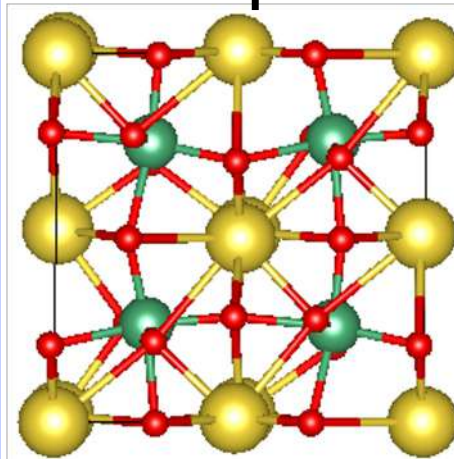
Pnma



a	3.896 Å	0.3%
b	3.850 Å	0.4%
c	3.913 Å	-0.1%

$$P = [0.0, 0.0, 0.0]$$

Pmc2_1



a	3.878 Å	0.8%
b	3.840 Å	0.6%
c	4.009 Å	-2.4%

$$P = [0.0, 0.4, 0.4]_g$$

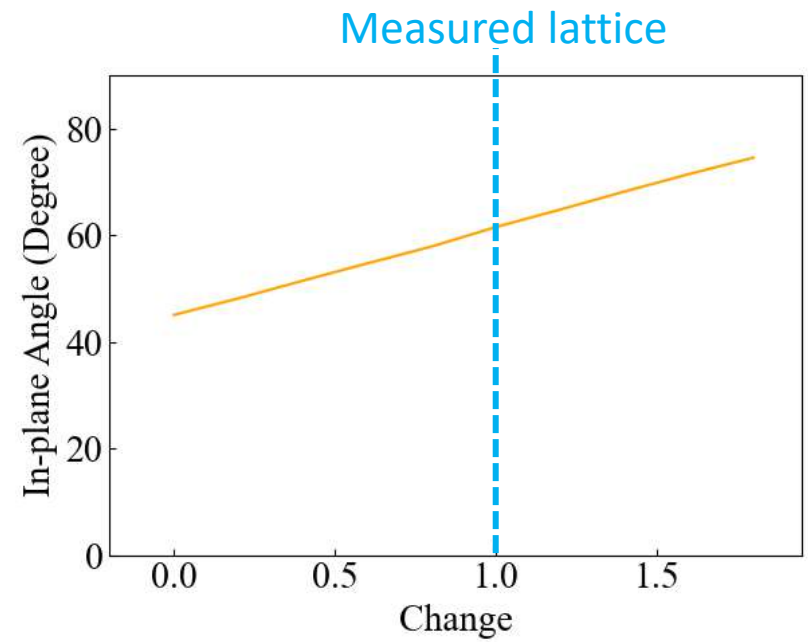
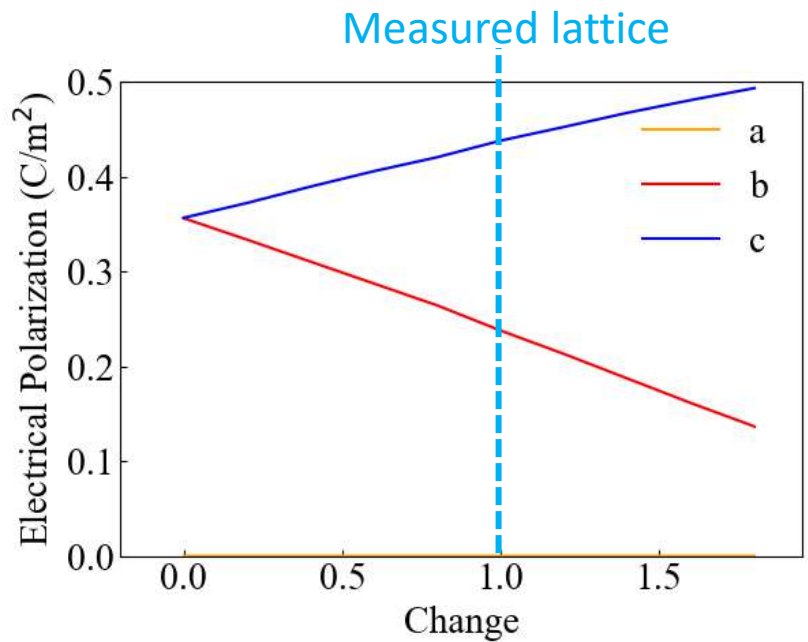
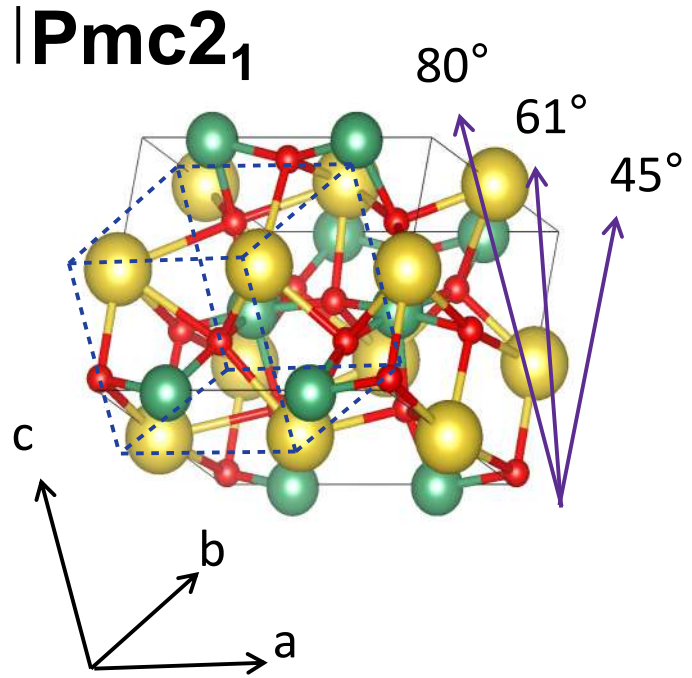
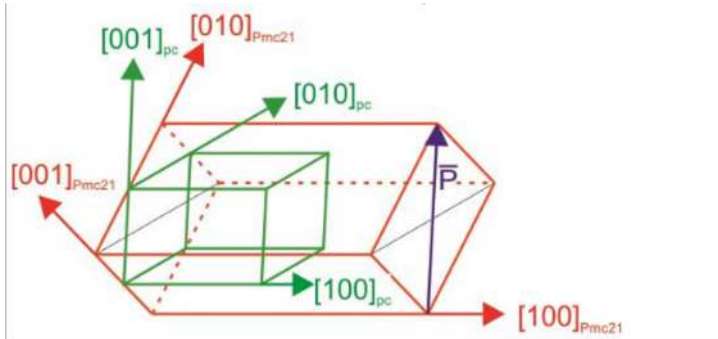


Investigation of Proposed Phases

Compressive strain
|NaNbO₃/NdGaO₃

- Orthorhombic structure
- Electrical polarization
- Out-of-plane direction [001]

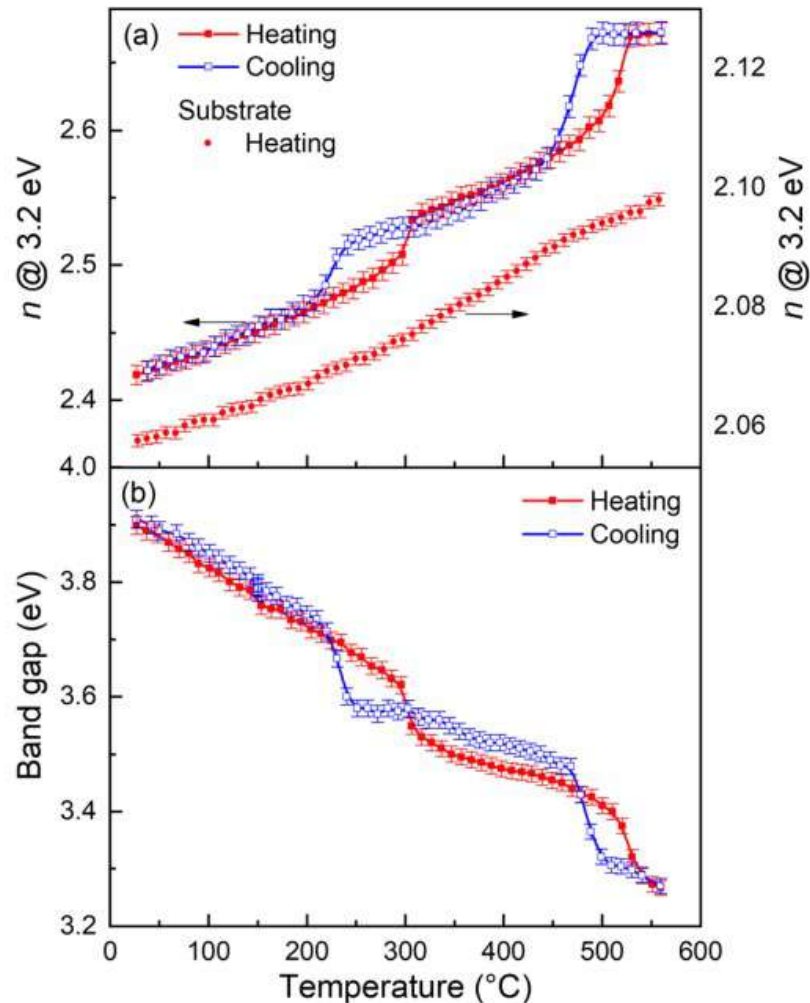
a	3.861 Å
b	3.855 Å
c	3.94 Å





Tensile strain

$\text{NaNbO}_3/\text{DyScO}_3$



| 300K

Space group (Pm) with in-plane polarization

| 350K

Space group (maybe, Pmm2) with in-plane polarization

| 500K

Space group (maybe, Pmmm) with no polarization

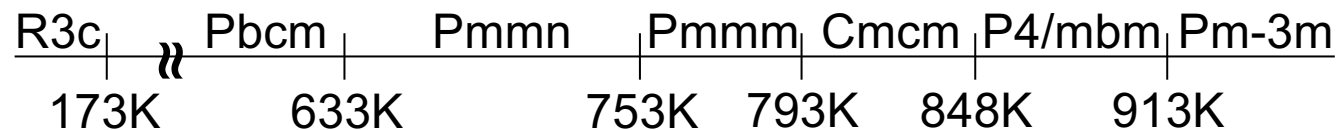
We don't have any information of Pmm2 and Pmmm phases.

How can we effectively investigate all different phases?



Phase Transitions Study for NaNbO_3

Phase diagram of perovskite NaNbO_3



Polarization sensitively depends on the atomic structure

→ Symmetry, lattice parameters, even displacement

OK inaccuracy: Missing thermodynamic effects

→ Ab initio Molecular Dynamics: Accurate but challenging

Can **machine learned interatomic potential** be a solution?

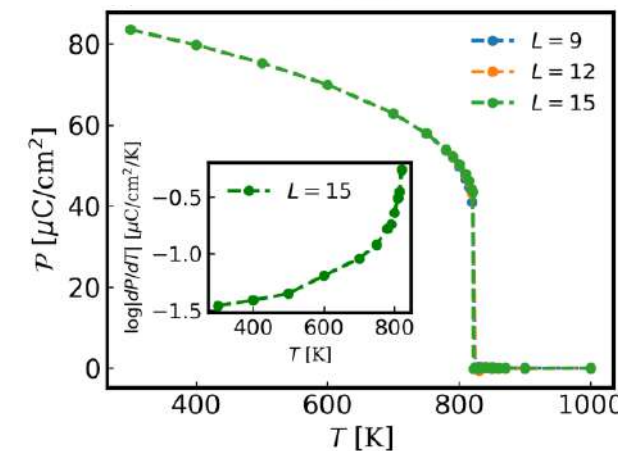
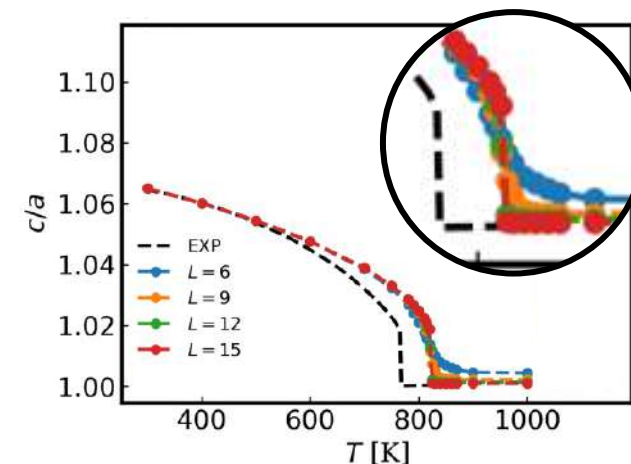
→ How can we guarantee the accuracy of this approach?

→ **Uncertainty estimation:** Lu's Silicon study

Phase transition of PbTiO_3

Using machine learned interatomic potential

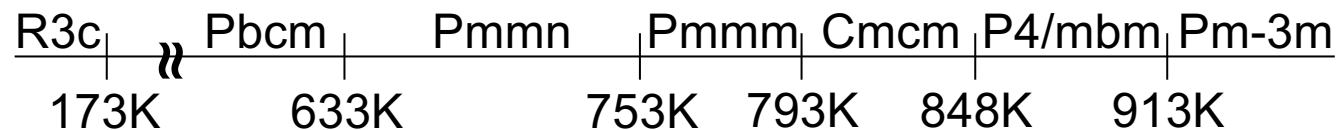
[2] P. Xie *et al.* arXiv:2205.11839 (2022)





Phase Transitions Study for NaNbO_3

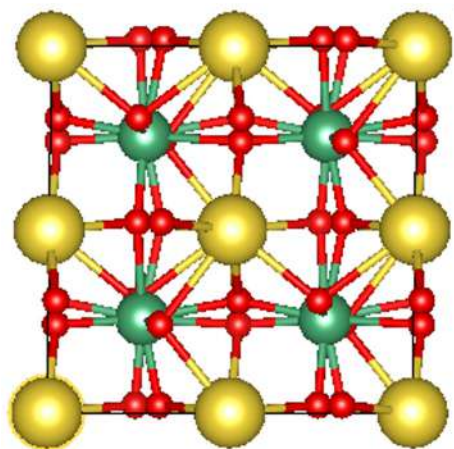
Phase diagram of perovskite NaNbO_3



Goal:

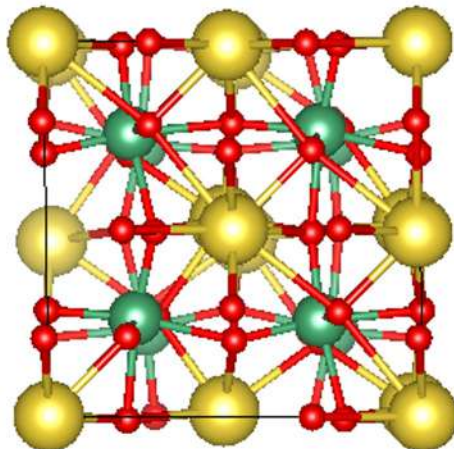
Ab initio Molecular Dynamics assisted with **machine learned interatomic potential** might **actively** investigate all different phases and their phase transitions

R3c



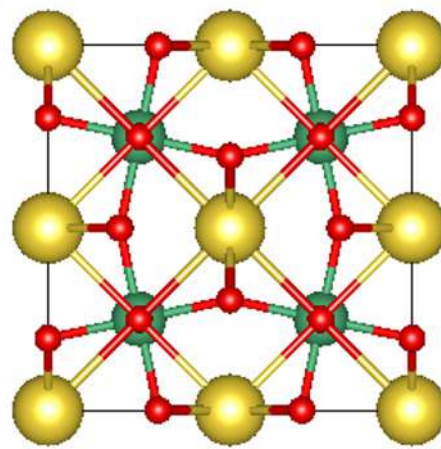
$$P = [0.3, 0.3, 0.3]$$

Pbcm



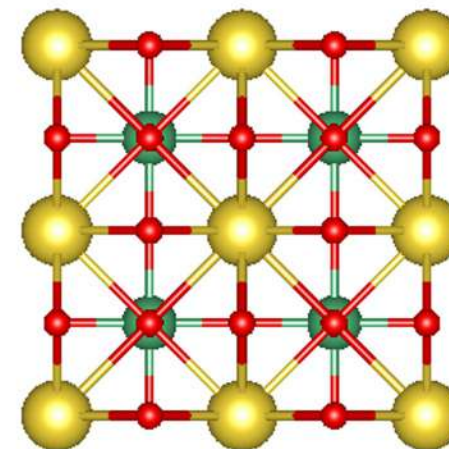
$$P = [0.0, 0.0, 0.0]$$

P4mbm



$$P = [0.0, 0.0, 0.0]$$

Pm-3m

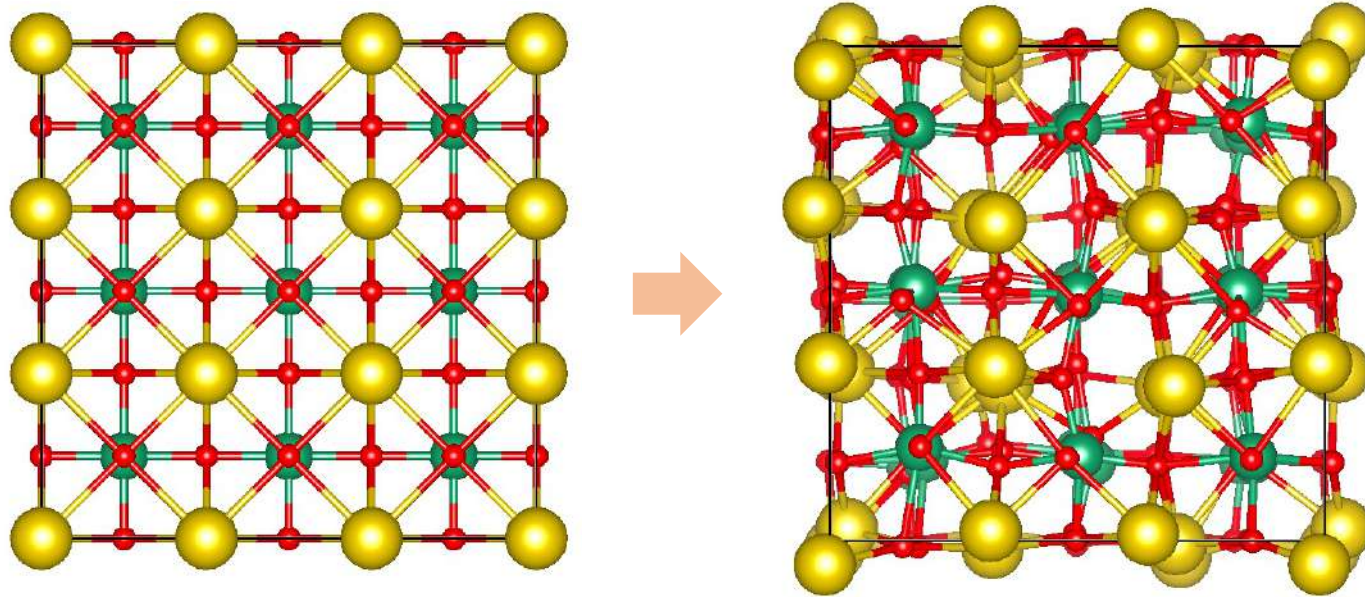


$$P = [0.0, 0.0, 0.0]$$

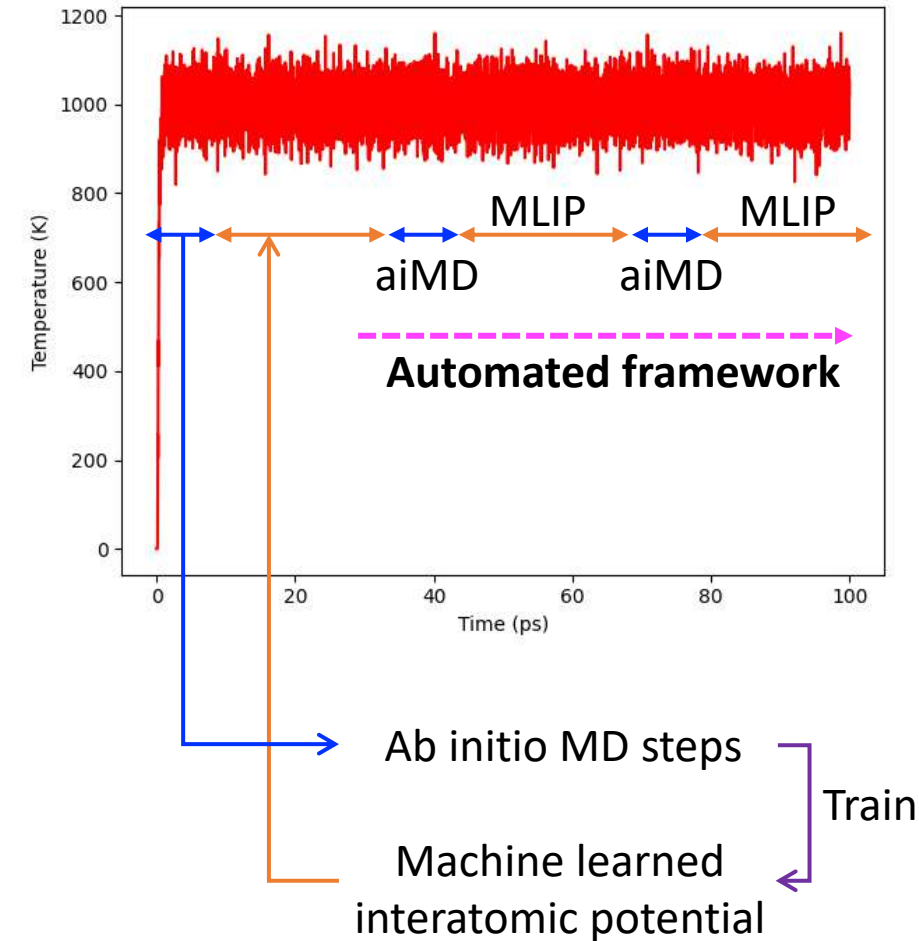
Machine Learning Potential with Active Learning

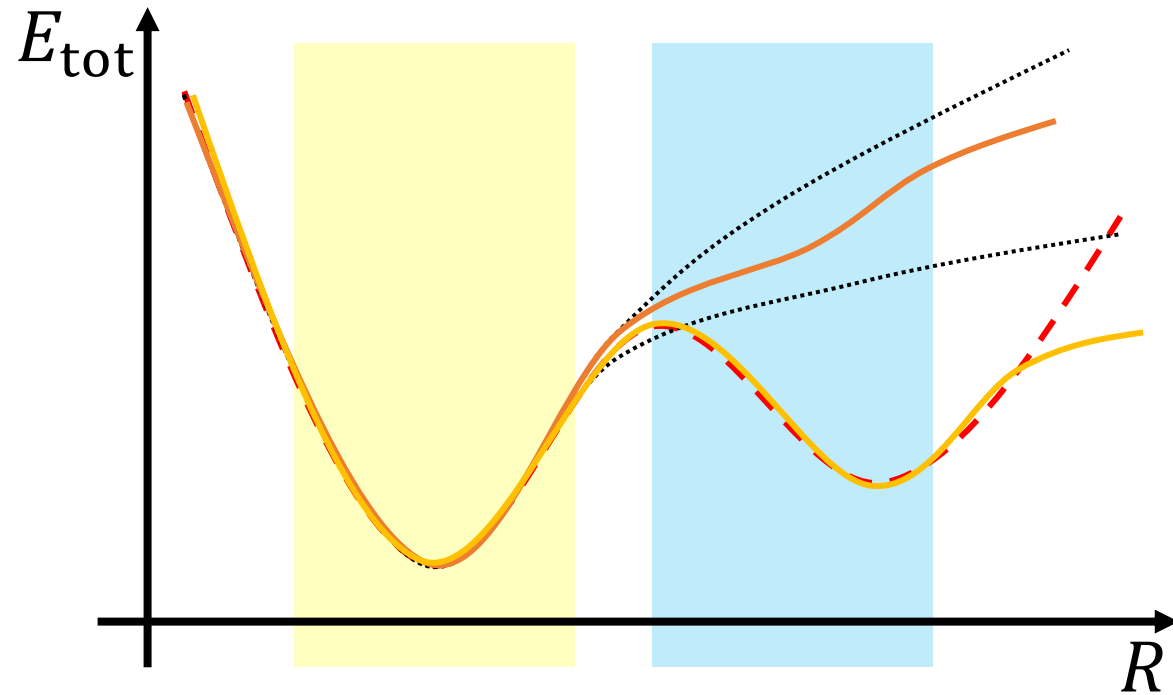


| Might need **long enough trajectory** and **large supercell** for *ab initio* molecular dynamics



→ If it is too large, need to find an alternative way
→ Machine learned interatomic potential (MLIP)





- - - : Real interatomic potential
- : ML Uncertainty
- : Trained MLIP
- : Retrained MLIP
- : First sampling range
- : Second sampling range

1. Calculate a ground state
2. Sample data around the ground state
3. Train many ML interatomic potentials (MLIP)
 - Might need different ML models
4. Check an uncertainty of trained models
 - **Epistemic uncertainty**
 - Aleatoric uncertainty
5. Sample additional data around that point
6. Retrain the MLIP with additional data



| Summary

- Investigate the spontaneous polarization in different phases of perovskite NaNbO_3
 1. Use the **electrical polarization** with the lattice information
 - **Identify** the phase of NaNbO_3 thin film structures with compress and tensile strains
 2. Automated investigation of phases by MD with **machine learned** interatomic potential
 - Enable the effective investigation of large enough supercell with long trajectory

| Expected outcomes

- Construct the phase diagram of strained NaNbO_3
- Use *aiMD* assisted with machine learned interatomic potential
 - Charge transport
 - Thermal conductivity
 - Thermoelectric efficiency

