## # Possibility of Superconductivity and Functional Electronic States at Ferroelastic Domain Boundaries in Cu/S–$Pb_3(PO_4)_2$

During our investigation of decades of accumulated research on ferroelastic domains and domain boundaries, we identified a highly intriguing research direction.

Ferroelastic domain boundaries are not merely interfaces separating two crystalline regions.

They can serve as functional spaces in which strain, dopants, charge carriers, and local polarity interact, potentially generating electrical conductivity, magnetic responses, photoelectric properties, and even superconducting states that do not exist in the bulk material.

Based on these previous studies, we are investigating the hypothesis that semiconducting functionality and localized superconducting states may emerge at the ferroelastic domain boundaries of Cu- and S-incorporated $Pb_3(PO_4)_2$.

## # Functionality of Ferroelastic Domain Boundaries

Ferroelastic domain boundaries can exhibit physical and chemical properties distinct from those of the bulk material.

Large strain and strain gradients are concentrated at the center of a domain boundary, potentially producing local symmetries and atomic arrangements that differ from the average bulk structure.

Because domain boundaries can have chemical potentials and defect formation energies different from those of the bulk, particular dopants, oxygen vacancies, and lattice defects may preferentially migrate to or become stabilized at these boundaries.

Dopants and defects concentrated at domain boundaries can modify atomic oxidation states, charge distributions, carrier concentrations, bonding environments, and spin states.

Such local electronic reconstruction may generate polarity, electrical conductivity, magnetic responses, photoelectric properties, semiconducting functionality, and superconducting states that are absent from the bulk material.

## # Reported Superconducting Cases in Ferroelastic Systems

In oxygen-deficient $WO_{3-x}$, highly conductive twin walls distinct from the bulk were observed, and sheet superconductivity at approximately 3 K was reported at these domain walls.

In $WO_3$ exposed to Na vapor, Na was also observed to preferentially migrate and accumulate along the twin walls.

This provides direct evidence that ferroelastic domain boundaries can act both as migration pathways for dopants and as regions of local dopant enrichment.

In separate studies of sodium tungsten bronzes, bulk superconductivity in $Na_xWO_3$ was first reported at approximately 0.57 K.

In surface Na-doped $WO_3$, localized superconducting islands measuring approximately 20–150 nm were observed below about 91 K. These regions occupied approximately 10% of the sample surface, while the remaining regions retained insulating behavior.

In oxygen-deficient $WO_{2.90}$, candidate signatures of filamentary superconductivity were reported near 80 K, and the characteristic temperature increased to approximately 94 K following Li intercalation.

The researchers interpreted these localized states as being associated with crystallographic shear planes enriched in charge carriers.

Together, these studies demonstrate that spatially confined structural regions enriched with dopants and defects can provide a platform for localized superconducting states that do not fully percolate throughout the bulk material.

## # Why We Focus on $Pb_3(PO_4)_2$

$Pb_3(PO_4)_2$ is a representative ferroelastic material that undergoes a structural phase transition at approximately 453 K, from a high-temperature trigonal phase to a low-temperature monoclinic phase, forming ferroelastic twin domains.

Studies by Salje and colleagues have shown that the domain boundaries in $Pb_3(PO_4)_2$ form nanometer-scale local structural regions that can possess structural and chemical properties different from those of the average bulk structure.

In Salje's 2012 comparative data, the total twin-wall thickness, (2w), of $Pb_3(PO_4)_2$ was summarized as approximately 0.8 nm by TEM and less than 1.3 nm by X-ray diffraction.

Although bulk $Pb_3(PO_4)_2$ is a centrosymmetric, nonpolar ferroelastic material,

local polarity absent from the bulk was directly observed at the W and W′ domain boundaries.

It was also reported that the introduction of $Ca^{2+}$ and $Mg^{2+}$ significantly increased the second-harmonic-generation signal from the domain boundaries, indicating enhanced local polarity.

These findings provide important precedent demonstrating that the functionality of $Pb_3(PO_4)_2$ domain boundaries can be controlled through elemental incorporation.

## # Our Hypothesis for Cu/S–$Pb_3(PO_4)_2$

Based on these previous studies, we are investigating the following hypothesis.

When Cu and S are incorporated into $Pb_3(PO_4)_2$, some of the dopants and associated defects may become selectively concentrated at the ferroelastic domain boundaries.

Cu/S incorporation may alter the local coordination environments, oxidation states, charge distributions, and carrier states of Pb and Cu.

Changes in the bonding environment induced by Cu/S incorporation may affect the local polarity and internal electric fields formed at the domain boundaries.

The incorporation of Cu and S may also modify the rotation of $PO_4$ tetrahedra, Pb–O and Cu–O coordination, oxygen bond angles and bond lengths, and the monoclinic lattice distortion.

If these structural distortions and electronic-state reconstructions become concentrated at the domain boundaries, they may generate low-dimensional conduction pathways, nonlinear electrical transport, functional semiconducting properties, and localized superconducting states that are distinct from the bulk material.

Our central hypothesis can therefore be stated as follows:

The ferroelastic domain boundaries of Cu/S-incorporated $Pb_3(PO_4)_2$ provide a functional space in which strain, local polarity, dopants, and charge carriers interact, potentially enabling semiconducting functionality and localized superconductivity.

We are currently investigating Cu/S-incorporated $Pb_3(PO_4)_2$ in which no crystalline secondary phase was detected by X-ray diffraction, using analyses of crystal structure, chemical bonding states, electrical transport, magnetic properties, and electronic structure.

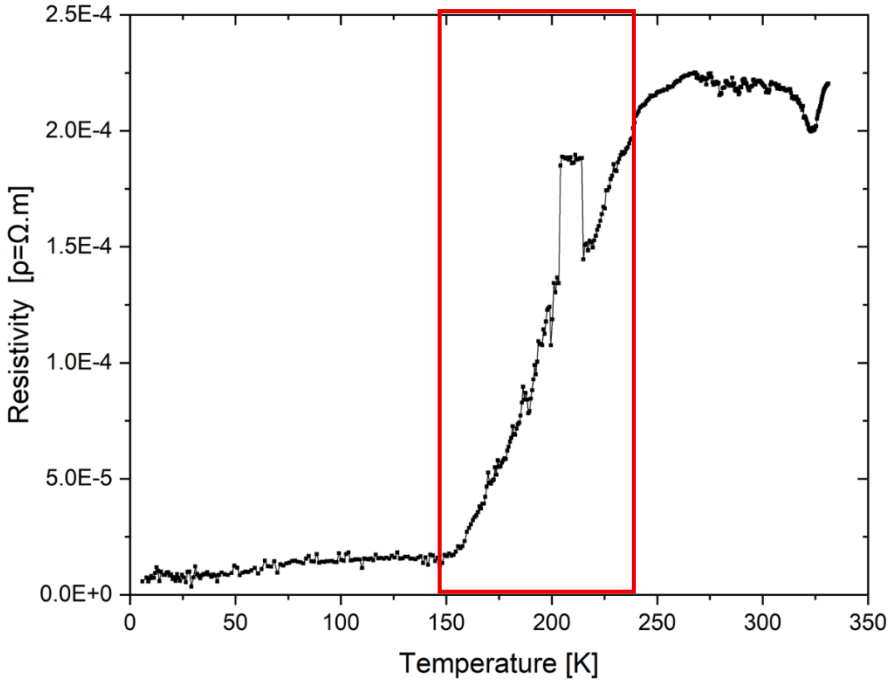
Based on the structural distortion, nonlinear conduction transitions, temperature-dependent hysteresis, and weak magnetic responses observed in bulk samples, we are studying the electronic states associated with the domain boundaries.

In subsequent thin-film studies, we plan to verify the spatial correlation between the domain structure and local conduction pathways.

We regard ferroelastic domain boundaries not simply as crystalline defects, but as a low-dimensional materials platform through which new conductive, polar, magnetic, and superconducting functionalities may be designed.

# # Major Experimental Results to Date

Resistance Drop at 150–220 K




The resistance-drop region was fitted using the percolation model

**ρ(T)=A(T−T c ) t +ρ 0** The fitting produced the following values: T c ≈157.5K / t≈1.22 /$R^2$ ≈0.91

A percolation exponent of approximately 1.22 lies within the low-dimensional percolation range associated with one- to two-dimensional behavior, within experimental uncertainty.

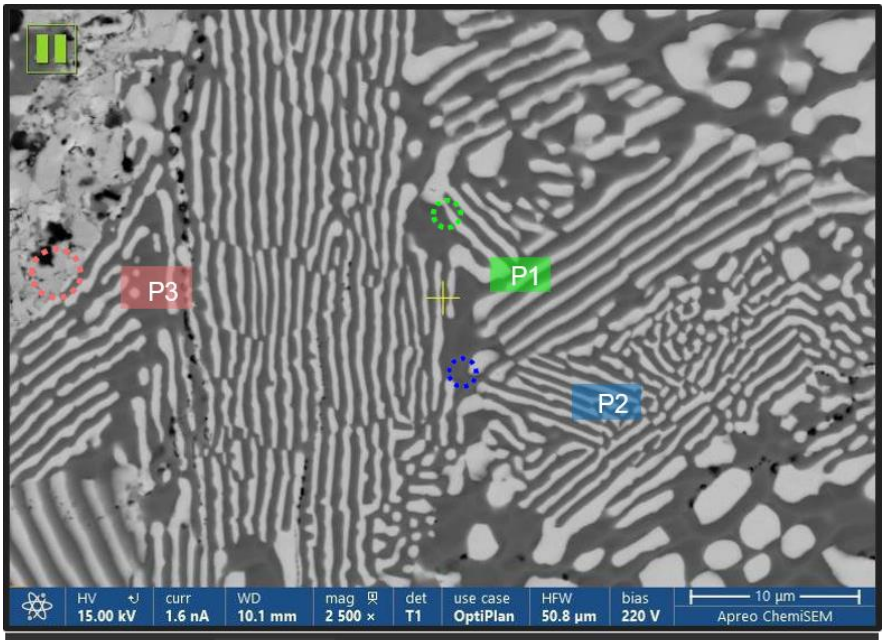
Mathematically, this suggests that the observed electrical-transport behavior is compatible with low-dimensional conduction pathways and is consistent with the hypothesis of conductive channels along domain boundaries.

The observed percolative transition may be considered a candidate superconducting critical-temperature feature, but it may also be explained by domain-related avalanche dynamics.

Nevertheless, the resistivity following the resistance drop reaches approximately (1\ \mu\Omega\cdot\mathrm{m}), corresponding to a semimetallic resistivity range.

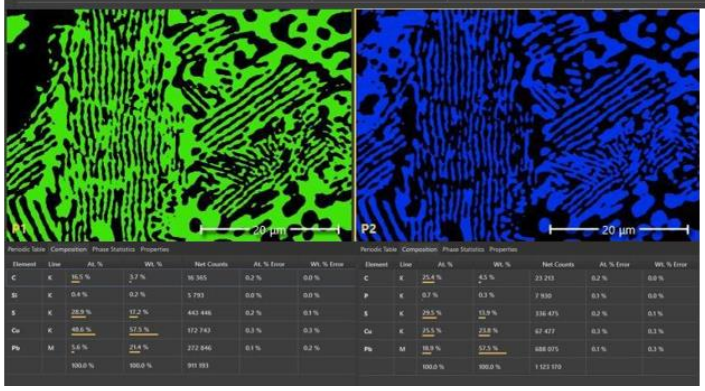
Previous studies have shown that complete zero resistance may not be observed when superconducting channels at domain boundaries do not fully percolate throughout the sample. Considering these findings, the possibility of localized superconductivity cannot be ruled out.

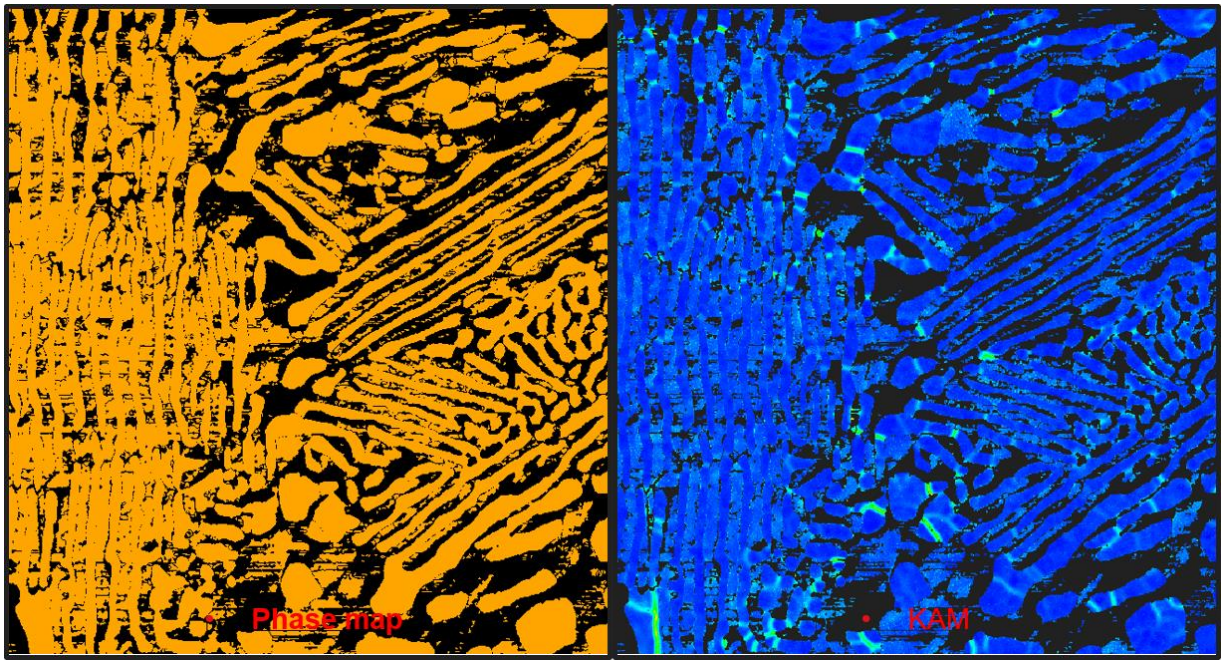
## Crystallographic Indications in the Resistance-Drop Sample




Periodic Table | Composition | Phase Statistics | Properties

| Name | Color | Area (µm²) | Area (px) | Area % | Component |
|---|---|---|---|---|---|
| Phase 1 (P1) | | 879.5 | 201 008 | 51.12 % | C1 |
| Phase 2 (P2) | | 810.7 | 185 286 | 47.12 % | C2 |
| Phase 3 (P3) | | 30.3 | 6 922 | 1.76 % | C3 |






SEM analysis revealed a crystallographic lamellar structure associated with ferroelastic domains in the sample exhibiting the resistance drop.

The phase and kernel average misorientation (KAM) analyses were consistent with the expected characteristics of ferroelastic domains.

In addition, the tendency of the Kikuchi-pattern and grain misorientation angles to become concentrated near characteristic angles of approximately 30° and 60° is consistent with the crystallographic characteristics of ferroelastic twinning.

## References

1. G. F. Nataf, E. K. H. Salje, and B. Casals, eds., Ferroelastic Materials, IOP Publishing (2025). ISBN 978-0-7503-6089-0.

https://store.ioppublishing.org/page/detail/Ferroelastic-Materials/?k=9780750360890

2. E. K. H. Salje, S. A. Hayward, and W. T. Lee, “Ferroelastic Phase Transitions: Structure and Microstructure,” Acta Crystallographica Section A 61, 3–18 (2005).

https://doi.org/10.1107/S0108767304020318

3. E. K. H. Salje, “Ferroelastic Materials,” Annual Review of Materials Research 42, 265–283 (2012).

https://doi.org/10.1146/annurev-matsci-070511-155022

4. A. Aird and E. K. H. Salje, “Sheet Superconductivity in Twin Walls: Experimental Evidence of $WO_{3-x}$,” Journal of Physics: Condensed Matter 10,

L377–L380 (1998).

https://doi.org/10.1088/0953-8984/10/22/003

5. A. Aird and E. K. H. Salje, “Enhanced Reactivity of Domain Walls in $WO_3$ with Sodium,” European Physical Journal B 15, 205–210 (2000).

https://doi.org/10.1007/PL00011037

6. Ch. J. Raub, A. R. Sweedler, M. A. Jensen, S. Broadston, and B. T. Matthias, “Superconductivity of Sodium Tungsten Bronzes,” Physical Review Letters 13, 746–747 (1964).

https://doi.org/10.1103/PhysRevLett.13.746

7. S. Reich, G. Leitus, Y. Tssaba, Y. Levi, A. Sharoni, and O. Millo, “Localized High-(T_c) Superconductivity on the Surface of Na-Doped $WO_3$,” Journal of Superconductivity 13, 855–861 (2000).

https://doi.org/10.1023/A:1007867710512

8. A. Shengelaya, K. Conder, and K. A. Müller, “Signatures of Filamentary Superconductivity up to 94 K in Tungsten Oxide $WO_{2.90}$,” Journal of Superconductivity and Novel Magnetism 33, 301–306 (2020).

https://doi.org/10.1007/s10948-019-05329-9

9. B. Wruck, E. K. H. Salje, M. Zhang, T. Abraham, and U. Bismayer, “On the Thickness of Ferroelastic Twin Walls in Lead Phosphate $Pb_3(PO_4)_2$: An X-Ray Diffraction Study,” Phase Transitions 48, 135–148 (1994).

https://doi.org/10.1080/01411599408200357

10. H. Yokota, S. Matsumoto, E. K. H. Salje, and Y. Uesu, “Polar Nature of Domain Boundaries in Purely Ferroelastic $Pb_3(PO_4)_2$ Investigated by Second Harmonic Generation Microscopy,” Physical Review B 100, 024101 (2019).

https://doi.org/10.1103/PhysRevB.100.024101

11. H. Yokota, S. Matsumoto, N. Hasegawa, E. K. H. Salje, and Y. Uesu, “Enhancement of Polar Nature of Domain Boundaries in Ferroelastic $Pb_3(PO_4)_2$ by Doping Divalent-Metal Ions,” Journal of Physics: Condensed Matter 32, 345401 (2020).

https://doi.org/10.1088/1361-648X/ab8b9b

12. G. F. Nataf and E. K. H. Salje, “Avalanches in Ferroelectric, Ferroelastic and Coelastic Materials: Phase Transition, Domain Switching and Propagation,” Ferroelectrics 569, 82–107 (2020).

https://doi.org/10.1080/00150193.2020.1791662

13. E. K. H. Salje, E. Dul'kin, and M. Roth, "Acoustic Emission during the Ferroelectric Transition Pm(\bar3)m→P4mm in $BaTiO_3$ and the Ferroelastic Transition R(\bar3)m→C2/c in $Pb_3(PO_4)_2$," Applied Physics Letters 106, 152903 (2015).https://doi.org/10.1063/1.4918746