

Measuring and Controlling the Electronic Transport Properties of BaZrS₃ Chalcogenide Perovskite Thin Films



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1. Introduction / Overview

- BaZrS₃ is a chalcogenide perovskite semiconductor of interest for optoelectronic applications in the VIS-NIR
- Relatively new material lacking comprehensive electronic properties characterization
- Goal:** Characterize transport properties using temperature-dependent Hall effect measurements, to inform materials processing in support of future device development

This Work:

- ~30nm thick BaZrS₃ films grown by gas-source molecular beam epitaxy (MBE) on LaAlO₃ substrates ($T_{\text{growth}} = 1000^\circ\text{C}$)
- n -type behavior with large sample-to-sample variation:
 - $n: 10^{19} - 10^{21} \text{ cm}^{-3}$
 - $\mu: < 0.5 \text{ cm}^2/\text{Vs} - 10 \text{ cm}^2/\text{Vs}$
- Suspect V_s as dominant donor, observe oxygen sensitivity which we attribute to the large $[V_s]$

2. Temperature-Dependent Hall

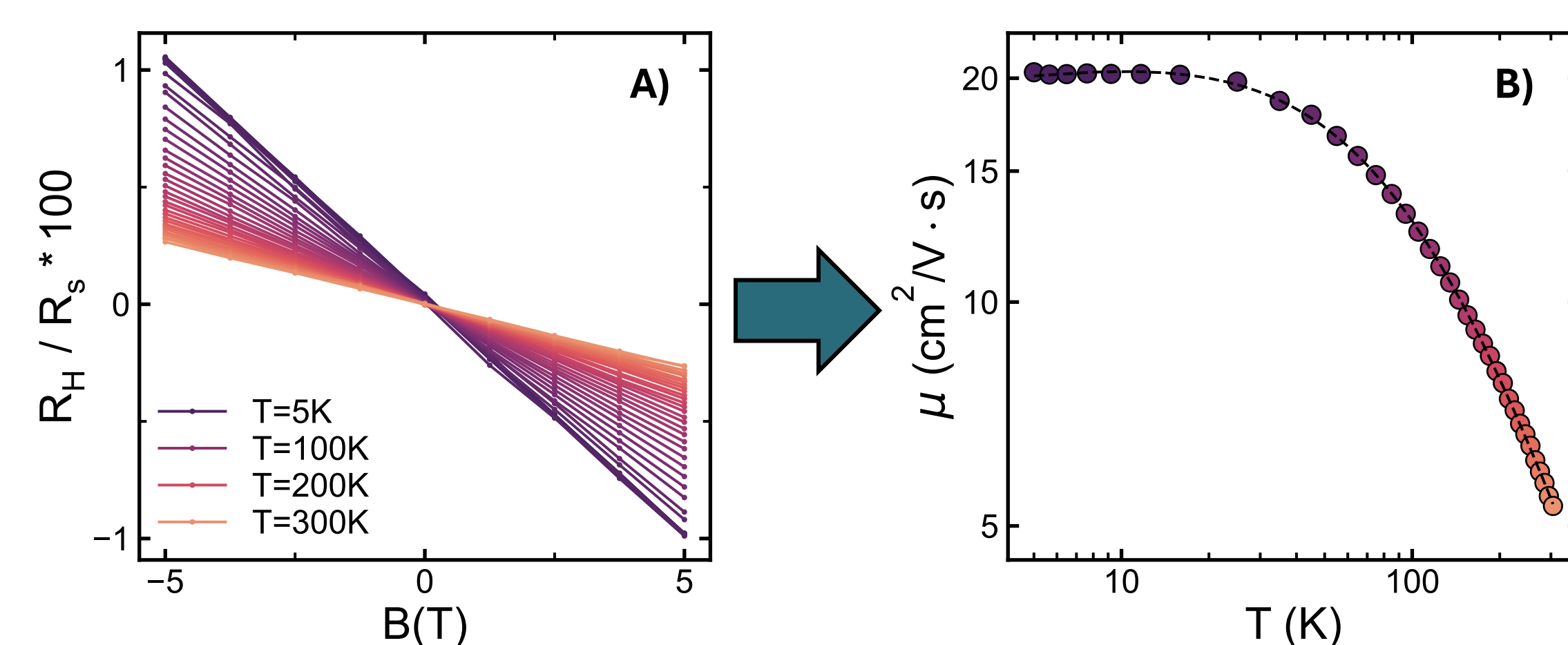


Figure 1: Hall data from a representative sample showing **A)** ratio of Hall resistance (R_H) to sheet resistance (R_s) as function of applied field at range of temperatures and **B)** temperature-dependent mobility obtained from fitting data in A).

- $\frac{d\mu}{dT} < 0$ suggests phonon scattering dominates at room temperature, agrees with theory predictions (Hautier @ Dartmouth) [1]
- At low temperatures $\mu(T)$ is flat, indicating neutral-impurity scattering as the mobility-limiting mechanism
- $\frac{d\mu}{dT} > 0$ (charged-impurity scattering) is not observed here, despite $n \sim 10^{20} \text{ cm}^{-3}$.
- Demonstrates tolerance of BaZrS₃ to charged defects

3. Mobility Trends

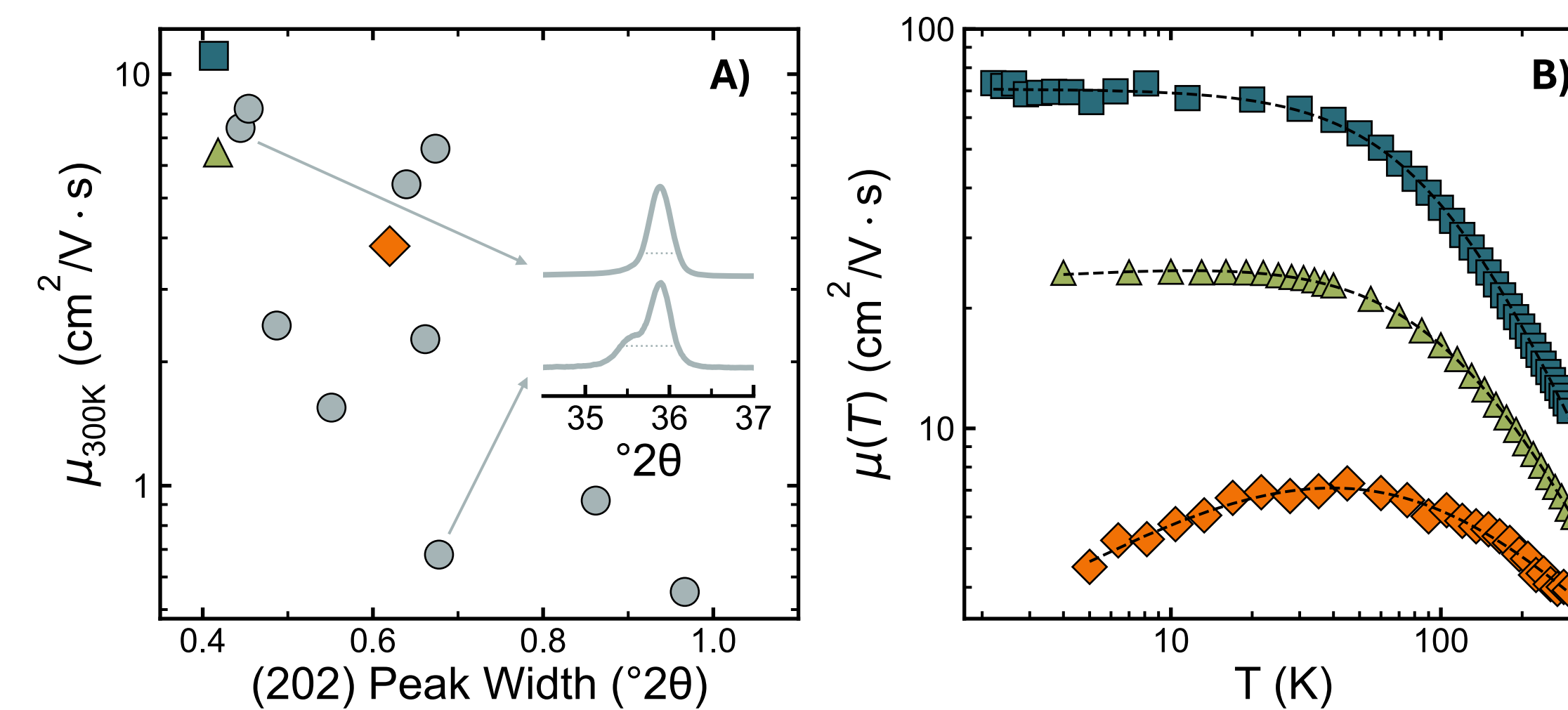


Figure 2: **A)** 300K electron mobility as function of BaZrS₃ (202) x-ray diffraction (XRD) peak full-width at one quarter height. Inset shows the normalized-intensity (202) peaks for two selected samples. **B)** Temperature-dependent mobility of select samples.

- Sharper XRD peaks correlate with larger μ , as expected
- Off-stoichiometry in BaZrS₃ accommodated by extended defects which appear as low-angle XRD shoulder [2], and are expected to degrade μ
- Low μ samples show onset of ionized-impurity scattering at low temperatures

4. Sample Instabilities

- Repeated measurements show R_s rises over time under ambient storage, despite no apparent film degradation
- Rate of R_s rise varies between samples, as fast as $(10\times)/(10 \text{ days})$
- 300 K Hall measurements show both μ and n decreasing, larger relative change in μ
- T -dependent Hall before/after storage shows consistent mobility-limiting mechanisms
- Results suggest **neutral impurity density has increased**

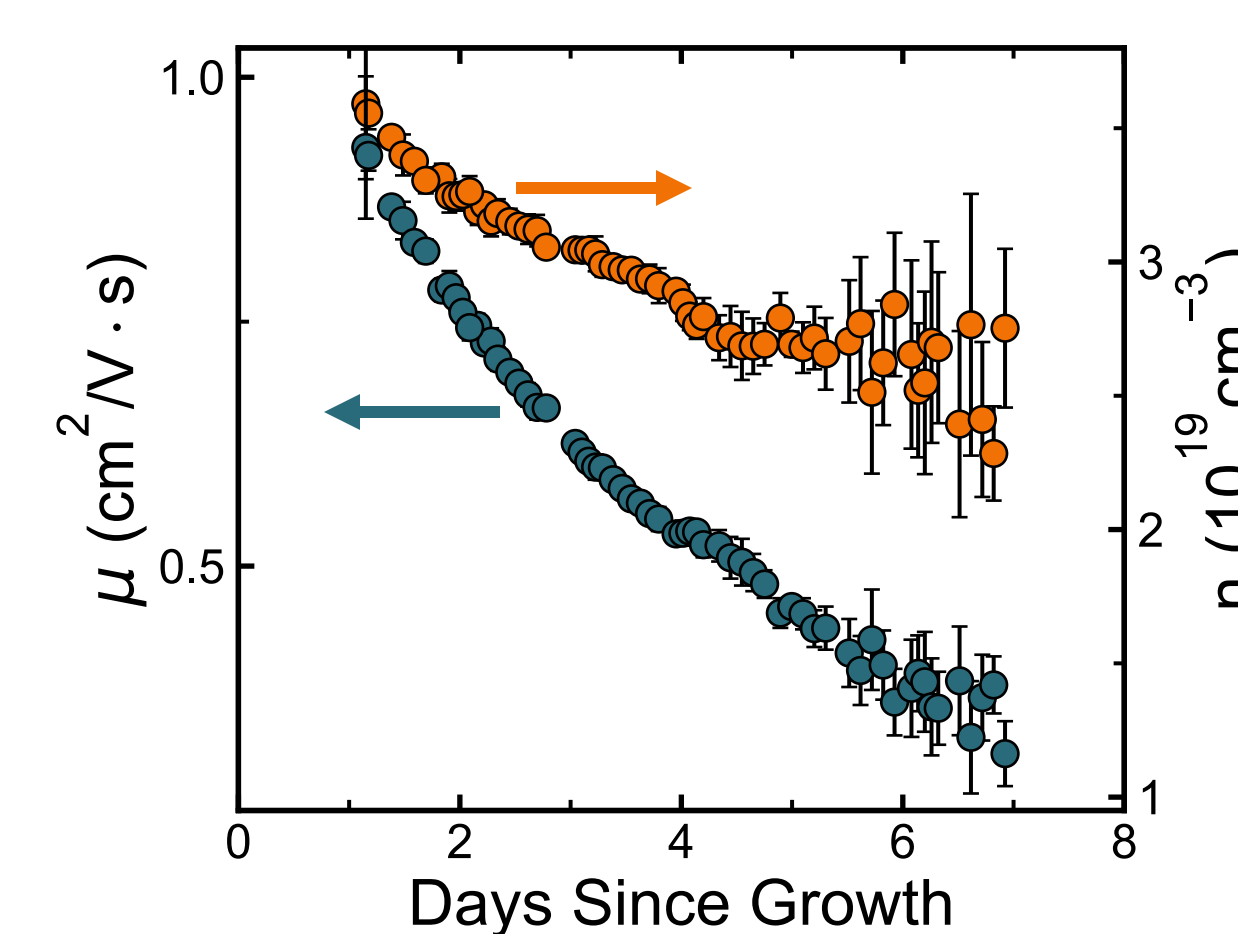


Figure 3: Repeated measurements of 300K electron mobility and density.

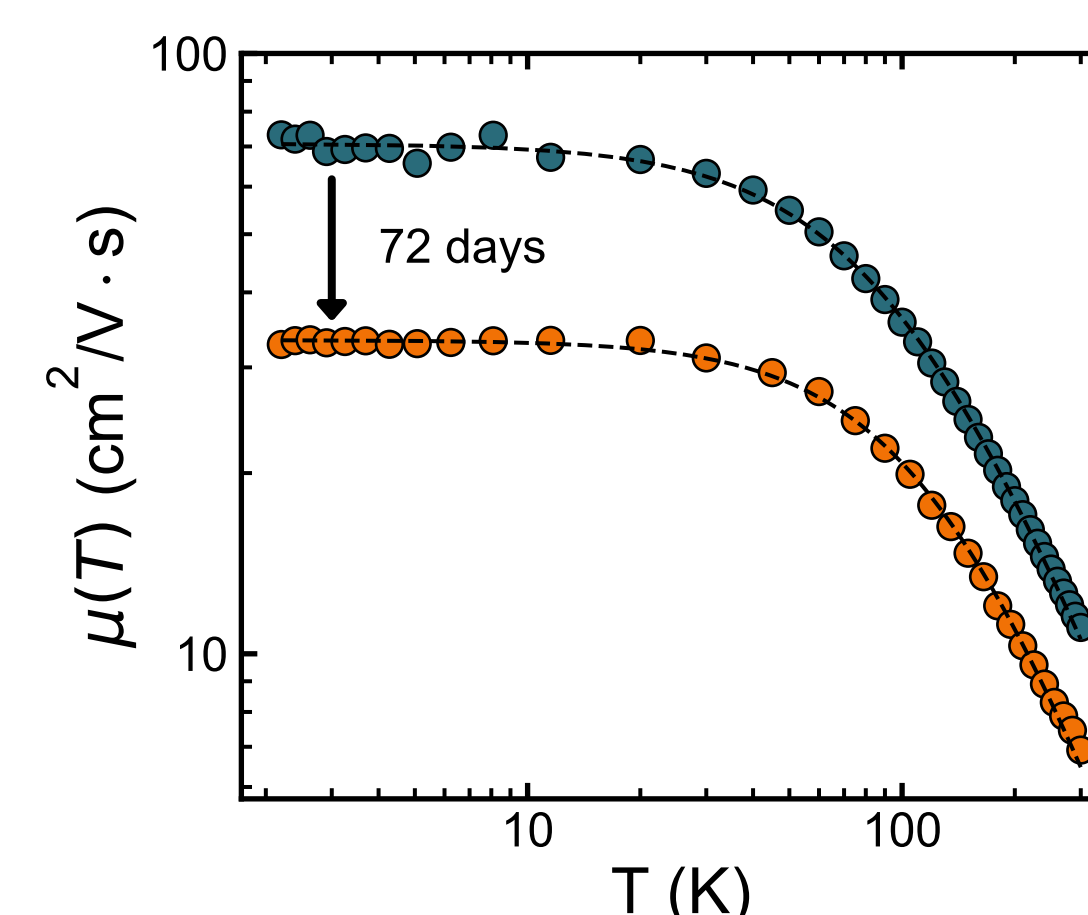


Figure 4: $\mu(T)$ measured shortly after growth (blue) vs remeasured after 72 days of ambient storage (orange).

5. Sulfur Vacancy Mechanism

- Hypothesize high $[V_s]$ allows rapid oxygen diffusion into film
- Oxygen reacts to convert V_s into O_s defects, predicted to be neutral in BaZrS₃ [1]
 - Decrease n
 - Increase neutral-impurity scattering
- Proposed mechanism supported by annealing experiments
 - Initial V_s population slowly filled with oxygen, R_s increases over time
 - Annealing creates new V_s , decreases R_s [3]
 - New V_s filled over time, R_s increases

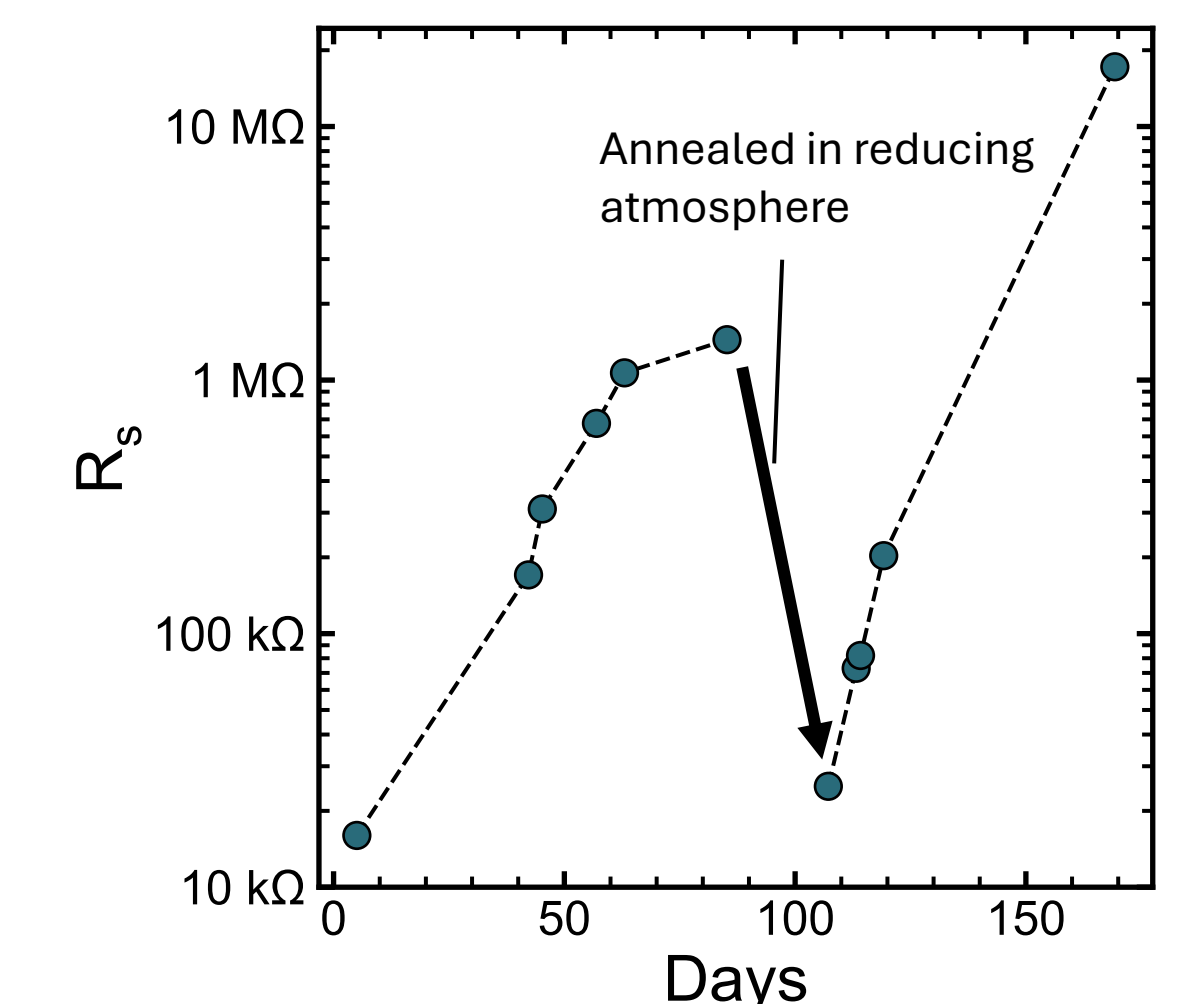


Figure 5: Four-point probe measured R_s over time. 400 C anneal in reducing atmosphere ($\text{H}_2 + \text{PH}_3$) performed at marked time

6. Outlook

- Large $[V_s]$ likely caused by high growth temperature of 1000°C
- Ongoing efforts to alter sample fabrication to...
 - Lower growth temperature** → expect different quenched-in defect population, lower as-grown $[V_s]$
 - Improve stoichiometry control** → reduced sample-to-sample variation
 - Increase sulfur activity** → lower as-grown $[V_s]$
 - Increase growth rate** → enable thicker films, less susceptible to effects of oxygen diffusion from top surface
- Obtaining controlled and stable electronic properties will enable more extensive future work
 - Doping studies to investigate doping concentration / type limits, following solid-state synthesis work in related materials [4]. Can BaZrS₃ be doped p -type?
 - Thin-film solar cell device fabrication and characterization
 - Investigate radiation hardness of BaZrS₃ electronic properties
 - Extend to BaZr(S,Se)₃ alloys with tunable band gap (1.4 – 1.9 eV) [2]

References

- [1] Z. Yuan et al., "Assessing Carrier Mobility, Dopability, and Defect Tolerance in the Chalcogenide Perovskite BaZrS₃," *PRX Energy*, vol. 3, no. 3, p. 033008, Sep. 2024, doi: 10.1103/PRXEnergy.3.033008.
- [2] I. Sadeghi et al., "Expanding the Perovskite Periodic Table to Include Chalcogenide Alloys with Tunable Band Gap Spanning 1.5–1.9 eV," *Adv. Funct. Mater.*, vol. 33, no. 41, p. 2304575, 2023, doi: 10.1002/adfm.202304575.
- [3] G. Aggarwal et al., "Charge Transport and Defects in Sulfur-Deficient Chalcogenide Perovskite BaZrS₃," May 27, 2024, arXiv:2405.17327, doi: 10.48550/arXiv.2405.17327.
- [4] K. Hanzawa et al., "Material Design of Green-Light-Emitting Semiconductors: Perovskite-Type Sulfide SrHS₃," *J. Am. Chem. Soc.*, vol. 141, no. 13, pp. 5343–5349, Apr. 2019, doi: 10.1021/jacs.8b13622.