Recrystallization Cycling and Quenching Study for the Synthesis and Characterization of Transition-Metal Dichalcogenides

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Background

Two-dimensional transition-metal dichalcogenides (TMDs) of the form MX_2 have unique optoelectronic properties when exfoliated down to molecular monolayers.

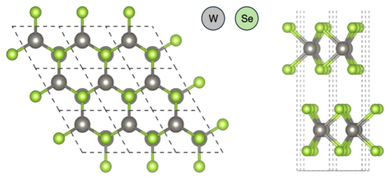

Figure 1. Top (left) and side (right) views of the atomic structure of WSe_2[5].

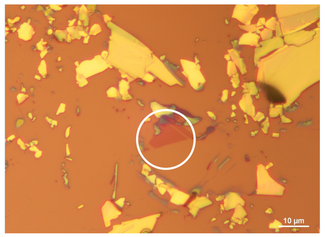

Figure 2. Monolayer WSe_2.

A two-step flux synthesis process reduces point defects in TMDs relative to standard methods, but results in small crystals with some defects still present.

Objectives:

- Recrystallization cycling process to further reduce point defect densities and produce larger crystals
- Investigate crystal growth dynamics via quenching and backlight imaging to maximize the efficiency of the synthesis process.

Methods

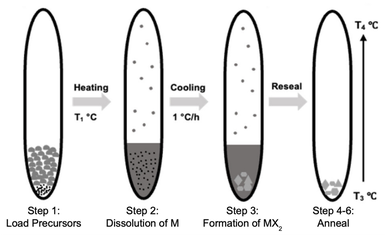

Figure 3. Two-step flux synthesis process.

- WSe_2 and $MoSe_2$ are synthesized using a two-step flux synthesis method as shown in Figure 3
- Additional Se is added and steps are repeated for recrystallization cycling

- Monolayers are exfoliated and transferred for scanning transmission electron microscopy (STEM) imaging
- Crystals are characterized using x-ray diffraction, Raman spectroscopy, and conductive atomic force microscopy (cAFM)

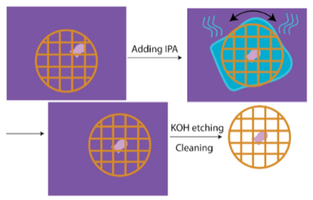

Figure 4. Isopropyl alcohol method for transferring monolayer to TEM grid.

Results

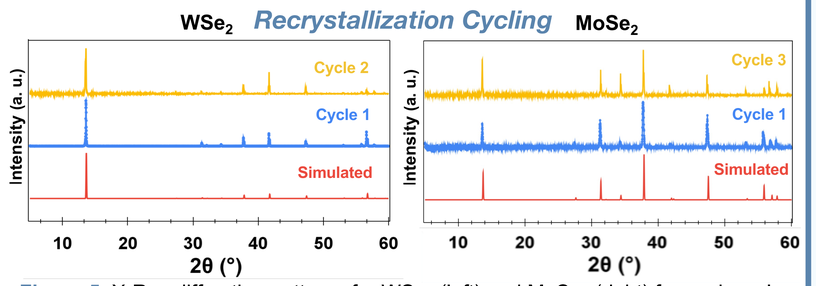

Figure 5. X-Ray diffraction patterns for WSe_2 (left) and $MoSe_2$ (right) for each cycle with simulated patterns.

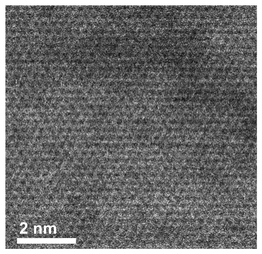

Figure 6. Scanning transmission electron microscopy (STEM) image of WSe_2.

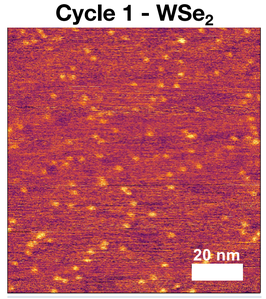

Table I. Defect density measurements for 2 cycles of WSe_2.

Cycle #	Defect Density (cm^{-2})
1	$1.1 \cdot 10^{12}$
2	$2.5 \cdot 10^{12}$

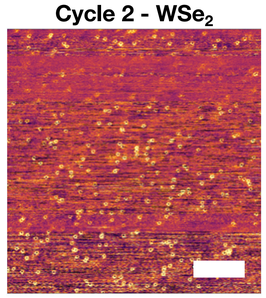

Figure 7. Conductive AFM 100 nm x 100 nm images for two recrystallization cycles.

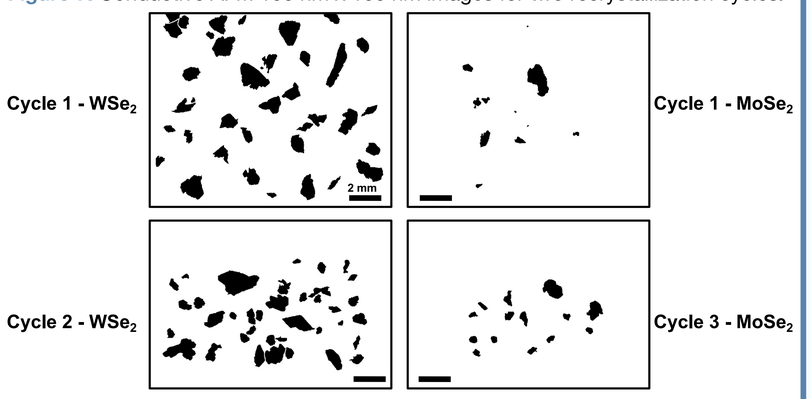

Figure 8. Binarized crystal images of WSe_2 for cycleas 1 and 2 and $MoSe_2$ for cycles 1 and 3.

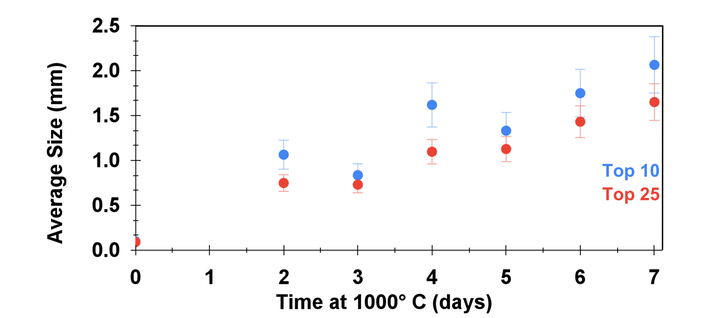

Figure 9. Averages of 10 and 25 largest crystals as a function of 1000˚C dwell time.

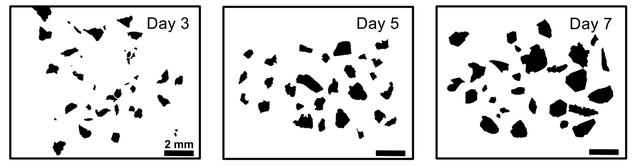

Figure 10. Binarized images of WSe_2 crystals for 3, 5, and 7-day 1000˚C dwells.

Conclusions/Future Work

- Using two-step flux WSe_2 powder as the metal precursor in additional cycles led to an increase in isovalent defect density
- Three-day dwells are sufficient to produce WSe_2 and $MoSe_2$ powder as confirmed by x-ray diffraction analysis, but a dwell time longer than three days is necessary to produce a significant number of usable crystals
- Dwell time and average crystal sizes of WSe_2 over the first seven days of dwelling are directly related
- Future studies are needed to investigate the relationship between dwell time and $MoSe_2$ crystal sizes, as well as whether cycling using fully formed crystals and longer dwell times produces larger crystals with less defects

Acknowledgements

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References: [1] Mak, K.F. *et al., Phys. Rev. Lett.*, ***105*** *(13), 138605 (2010).* [2] Rhodes, D. *et al., Nat. Mater.*, **18**, 541-549 (2019). [3] Liu, S. *et al., ACS Nano*, **17** (17), 16587–16596 (2023). [4] Li, Y. *et al., Mater. Res. Express,* **9**, 12201 (2022). [5] Han, D. *et al.* Chemical Trend of Transition-Metal Doping in WSe_2. https://www.osti.gov/servlets/purl/1564195