Liquid Salt Transport Growth of Single Crystals of the Layered Dichalcogenides MoS$_2$ and WS$_2$

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Supporting Information

ABSTRACT: The growth of single crystals of MoS$_2$ and WS$_2$ by materials transport through a liquid salt flux made from a low-melting mixture of NaCl and CsCl is presented. The crystals are structurally characterized by single-crystal X-ray diffraction, which reveals that the 2H-MoS$_2$ crystals contain a very small percentage (about 3%) of 3R intergrowths and that the 2H-WS$_2$ crystals display less than 1% of 3R intergrowths. Characterization of the crystals by scanning electron microscopy is presented as are photoluminescence spectra of exfoliated monolayers that show that MoS$_2$ crystals grown by this method are superior in quality to commercially available MoS$_2$ crystals and equivalent to the current state of the art.

INTRODUCTION

Transition metal dichalcogenides (TMDCs) are compounds with a composition MX$_2$ where M is a transition metal such as tungsten or niobium, and X is a chalcogen such as sulfur, selenium, or tellurium. TMDCs have been a subject of active study for several decades due to their wide variety of observed properties, including superconductivity,$^1$ charge density waves,$^2,3$ and photoluminescence.$^4,5$ In recent years, layered TMDCs such as MoS$_2$ have received intense focus not only due to their catalytic properties$^6,7$ but also for the ease with which they can be exfoliated into monolayers and the interesting properties that result.$^8,9,10$

A significant issue that has arisen in the study of MoS$_2$ is the difficulty of growing large, high-quality single crystals. For example, while MoS$_2$ monolayers can be reliably grown using chemical vapor deposition,$^11,12$ bulk growth has for the most part been achieved solely by the vapor transport method,$^{13,14}$ which often can produce a significant number of defects and atom deficiencies, resulting in different properties under slightly altered growth conditions.$^{15,16}$ In the case of MoS$_2$, in particular, a substantial amount of research work has been performed on the naturally occurring mineral form of the compound, which can result in dramatically varying properties depending on a number of uncontrollable factors.$^{17}$ Bearing this in mind, as well as that natural single crystals of MoS$_2$ are an exhaustible and nonrenewable resource, the search for additional crystal growth methods for this compound and others is an active field of research.

Recently, Zhang et al.$^{18}$ have published an alternative approach to the growth of bulk crystals of MoS$_2$, using a molten metal “solution transport” method, a horizontal flux analogous to the more common vapor transport method$^{19}$ that has been previously successfully applied to chalcogenide and pnictide crystal growth.$^{20,21}$ The resulting crystals, grown in tin metal flux, have many desirable properties. Here, in contrast, we describe a method for crystal growth that employs a low-melting mixture of NaCl and CsCl as a salt flux for layered MoS$_2$, eliminating the use of a metal flux, and extend the application of this technique to the closely related compound WS$_2$. Characterization of thin layers of MoS$_2$ crystals grown in this fashion in an optical device showed excellent photoluminescent properties—better than the commercial crystals commonly employed in research on this material and equivalent to the best crystals currently reported.

EXPERIMENTAL SECTION

Polycrystalline MoS$_2$ was synthesized by first mixing a stoichiometric amount of molybdenum powder (99.9%, Alfa Aesar) with a 5% excess of sulfur (99.5%, Johnson Matthey). The mixture was loaded into a sealed, evacuated quartz tube and heated to 950 °C at a rate of 60 °C/h. The tube was heated for 10 days and then cooled to room temperature over 24 h. The resulting material took the form of large, loosely packed clumps of crystalline MoS$_2$ with a distinct "glitter" appearance, although no single crystals could be isolated of sufficient size.

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quality for structural characterization. Polycrystalline WS$_2$ was similarly synthesized, with the substitution of tungsten powder (99.9%, Alfa Aesar) and a reaction temperature of 1000 °C, which resulted in a dull gray powder.

For single-crystal growth, a 100 mg pellet of polycrystalline MoS$_2$ or WS$_2$ was placed in a quartz tube of outer diameter 16 mm, wall thickness 0.8 mm, and approximately 7 cm in length (after sealing). A 10 g mixture of 38 mol % NaCl (99.0%, Alfa Aesar) and 62 mol % CsCl (99%, Alfa Aesar) was used to fill the remaining space in the tube. This salt mixture was chosen for a number of reasons; first, it forms a low-melting eutectic and is reliably liquid at temperatures above 600 °C, allowing for experimentation and crystal growth over a wide variety of temperature ranges and temperature gradients. Second, in comparison to other compounds commonly used for flux growth, such as LiCl and AlCl$_3$, both of these salts are quite air-stable and do not necessitate the use of a drybox for handling or storage. Finally, as the resulting mixture is highly water-soluble, removal and cleaning of the resulting crystals can be easily performed by washing with distilled water, without any need of mechanical separation, scraping, or centrifuging which can damage thin crystals or crystal surfaces.

The tube was sealed under a vacuum and placed in a small box furnace in a horizontal configuration, with the end containing the pellet pointed toward the back of the furnace and the growth end pointing toward the furnace door, thus using the natural temperature gradient in the furnace. The tube was then heated to 1000 °C (MoS$_2$) or 1100 °C (WS$_2$) at 90 °C/h. The molten flux covered the entire bottom of the tube, allowing for “liquid transport” analogous to the more common vapor transport crystal growth method. A diagram of this reaction orientation can be viewed in Figure 1. After 1 week, the tube was cooled to 650 °C at a rate of 2 °C/h. During cooling, the molten salt flux remained transparent, and crystals could be observed growing on the end of the tube closest to the furnace door. The tube was then removed from the furnace and quenched in a vertical configuration, with the end containing the resulting crystal structures can be seen in Figure 2. Crystallographic data and atomic positions for our MoS$_2$ and WS$_2$ can be found in the Supporting Information. Single-crystal refinement of WS$_2$ proved unexpectedly difficult, as crystals of sufficiently small size could not be readily obtained without

**RESULTS AND DISCUSSION**

**Crystal Structure and Physical Characterization.** Single-crystal X-ray diffraction patterns were measured for several planar single crystals of both MoS$_2$ and WS$_2$. The resulting crystal structures can be seen in Figure 2. Crystallographic data and atomic positions for our MoS$_2$ and WS$_2$ can be found in the Supporting Information. Single-crystal refinement of WS$_2$ proved unexpectedly difficult, as crystals of sufficiently small size could not be readily obtained without

**Figure 1.** Cartoon schematic of the orientation used in solution-transport crystal growth.

**Figure 2.** Crystal structures of salt-flux-grown MoS$_2$ and WS$_2$. (a) Crystal structure of MoS$_2$ as determined by single-crystal X-ray diffraction. Purple spheres represent Mo atoms, and yellow spheres represent S. Lighter-shaded purple and yellow spheres indicate minorly occupied Mo and S sites. (b) Crystal structure of WS$_2$ as determined by single-crystal X-ray diffraction. Gray spheres represent W atoms. Lighter-shaded gray and yellow spheres indicate minorly occupied W sites.
introducing strain or stacking faults to the system, resulting in a slightly large residual electron density. Crystallographic analyses from the positions of sharp Bragg reflections reveal that both compounds crystallize in the hexagonal space group \( P6_3/mmc \) (No. 194). Within the unit cells of both MoS\(_2\) and WS\(_2\), the refinements of the average structures (i.e., what the single-crystal diffraction patterns determine) show that there are two unique metal atom sites (Wyckoff sites 2\( b \) and 2\( c \)). The 2\( b \) site in both compounds is only slightly occupied (3.14% in MoS\(_2\) and 0.79% in WS\(_2\)), which is an indication of the presence of stacking faults. Similarly, the unit cells of MoS\(_2\) and WS\(_2\) exhibit two unique S atoms sites (Wyckoff sites 4\( e \) and 4\( f \)). The 4\( e \) site in MoS\(_2\) is 3.14% occupied, corresponding well to the fraction of Mo atoms in the 2\( b \) site. As these two values were refined independently and not fixed to each other, their agreement is significant. For WS\(_2\), where the scattering factor for S is small compared to that for W, and the fraction of misplaced W’s is very small (0.79%), the identification of the associated S position is not as clear as in the MoS\(_2\) case, and so its fractional site occupancy is fixed to be equal to that of the W that is out of place due to the stacking faults.\(^{27,28}\)

The SXRD patterns from three different planes (0\( k l \), h0l, and hkl) in the reciprocal lattice for both compounds are shown in Figure 3. Streaking, which would indicate the presence of a large fraction of stacking faults, is not clearly visible in these reciprocal lattice planes. This is consistent with the small fraction of stacking faults inferred from the structural refinements. Figure 4 contains an illustration of one possible type of stacking fault that would lead to the observed partially occupied sites in MoS\(_2\). The stacking faults as envisioned can be interpreted as an occasional intergrowth of 3R-MoS\(_2\) in an otherwise 2H structure.

Larger flakes of MoS\(_2\) and WS\(_2\) were inspected using SEM to determine whether they were true single crystals or merely well-defined agglomerations of smaller crystals. Images of two flakes of MoS\(_2\) can be seen in Figure 5, and one flake of WS\(_2\) is in Figure 6. The lack of visible boundaries or seams in the surfaces of the flakes suggests that these samples are single crystals. Small hexagon-like growth features (“islands”) can be observed on the surfaces of all MoS\(_2\) flakes studied. A close-up image some of these hexagonal features can be seen in Figures 5c and 7b. Figure 5c is of particular interest, as the hexagonal island has itself developed a similar feature on its surface. The flakes of WS\(_2\) do not appear to exhibit the same growth features. EDX measurements on several samples indicate that the flakes are pure MoS\(_2\) and WS\(_2\), respectively, and that no other elements are present in a measurable quantity.

Results from the Sn-based flux growth of MoS\(_2\) from Zhang et al.\(^ {18}\) indicated that their bulkier crystals result from screw-dislocation-driven (SDD) growth. As the mechanism of crystal growth is determined by a number of factors, including subtle differences in chemical potential, it is not necessarily the case...
In order to compare the growth mechanism of our samples, atomic force microscopy (AFM) measurements were performed on several regions of a single-crystal flake of MoS$_2$. Figure 7 depicts the results of AFM measurements on two regions of a crystalline flake; Figure 7c shows the surface of one of the hexagonal features, while Figure 7d depicts a striated triangular feature that was observed nearby. Figure 7a,b are optical and SEM images of the broader region, with specific areas of interest identified in Figure 7a by colored boxes. For clarity, Figure 7c was cropped and rotated, but images have otherwise not been manipulated. While striations are visible on the crystal surface, there is no evidence of the spiral-like patterns typically associated with SDD growth. The presence of the hexagonal features on the crystal surface suggests instead that our crystals form via surface nucleation growth, which may explain the thinner nature of our crystals in relation to the bulkier samples of Zhang et al. A flake of WS$_2$ examined via AFM can be seen in Figure 6c. WS$_2$ flakes do not display any of the small hexagonal features, nor any of the spiral patterns that are indicative of SDD growth. The precise growth mechanism of these crystals therefore remains ambiguous.

Characterization by Photoluminescence. In order to evaluate the intrinsic optical quality of the solution-transport-grown MoS$_2$, we prepared monolayers of MoS$_2$ by exfoliation and encapsulated between thin, insulating hexagonal boron nitride (hBN) on SiO$_2$ (285 nm)/Si substrate as shown in Figure 8a. Photoluminescence (PL) spectra were taken at $T = 4$ K on the hBN/MoS$_2$/hBN heterostructure, as well as on similar heterostructures composed of different MoS$_2$ crystals available from commercial vendors (HQ graphene and 2D semiconductor). The PL spectra of these heterostructures, shown in Figure 8b, exhibit narrow neutral exciton ($X^0$) emission at energies between 1.93 and 1.95 eV due to a different dielectric environment, with a line width varying, depending on the sample used and the detection spot position. Notably, the exciton line width of our solution-transport-grown MoS$_2$ is around 4 meV, comparable to chloride-assisted vapor transport-grown MoS$_2$ and three times sharper than that of either commercial sample (11.5 and 15.5 meV for HQ graphene and 2D semiconductor respectively). This sharper
excitonic emission in our monolayer MoS₂ suggests that our growth method can produce high optical quality without a pronounced degree of disorder that can lead to inhomogeneous broadening in the PL spectra.

**CONCLUSION**

Leaf-like single crystals of MoS₂ and WS₂ have been grown using a liquid-transport flux method, using a CsCl/NaCl eutectic salt in a horizontal configuration. Characterization in a heterostructure device shows that luminescence from the crystals displays a more narrow energy spread than those available commercially. Crystals of WS₂ are also grown by the same method. No clear signs of surface nucleation or screw-dislocation-driven growth are observed. Aside from the sulfide compounds described here, early experiments suggest that this method may also be successfully applied to the growth of single crystals of the related transition metal diselenides WSe₂ and MoSe₂.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.9b00785.

Document containing four tables of crystallographic refinements and results for MoS₂ and WS₂, and a powder XRD pattern for MoS₂.

**Accession Codes**

CCDC 1921982 and 1922046 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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**REFERENCES**


(28) WS2 crystal structure information. Occupancy of each site: W1 (2c): 0.9921(12). W2 (2b): 0.0079(12). S1 (4f): 0.99. S2 (4e): 0.01. Formula mass: 247.98 amu. Crystal system: hexagonal. Space group: P63/mmc. Unit cell dimensions: a = 3.1599(4) Å, c = 12.3554(17) Å, V = 106.84(2) Å³, T = 300(1) K. Z = 2, μ = 55.530 mm⁻¹. Final R indices (Rf, wRf) = 0.0119/0.0247.

