Tunable Spin Splitting in the Two-Dimensional Transition Metal Chalcogenides
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Spintronics is being explored for electronic control through regulated changes in magnetic polarity. Intrinsic properties of electrons are utilized to control the resulting magnetic fields generated by the material. In this study, stable two-dimensional germanium monochalcogenide (GeMC) crystals are synthesized to explore their potential as spintronic candidates. Synthesis efforts were focused on Janus Ge_2XY crystals, although the pure GeX (X, Y = S, Se, and Te) phases also proved viable candidates. Two synthesis techniques were used to grow each of the six materials: metallic flux and chemical vapor transport (CVT). Results indicate that two forms of stable binary 2D GeMC crystals can be synthesized reliably using CVT growth. The same technique produced evidence of a Janus Ge_2XY phase, indicating that synthesis of the ternary phases is possible. With reliable synthesis techniques, future resistivty and hall effect measurements will be used to explore the spintronic properties of these materials.

I. Background

Spintronics is a field of electronics where electron spin is manipulated to enhance modern computer performance. These devices require materials with ideal electrical and magnetic properties. Specifically, materials must exhibit strong spin-orbit coupling (SOC) as well as persistent spin texture (PST). SOC allows the magnetic moments associated with electrons to be properly oriented in response to a potential difference across a sample. However, materials with high SOC often lack the spin coherence needed to create well functioning spintronic devices. This is resolved by utilizing PST which supports long spin lifetimes of materials through uni-directional spin orientations. Computational research indicates that stable two-dimensional germanium monochalcogenides (GeMC) specifically Janus Ge_2XY and pure GeX (X, Y = S, Se, and Te) crystalline phases should exhibit natural PST. Moreover, the material exhibits a large SOC parameter where the PST sustains [1]. Experimentally exploring 2D GeMC will help optimize current spintronic devices, making them smaller, more efficient, and commercially viable.

II. Results: Metallic Flux Growths

Two experiments with self-flux were performed in alumina crucibles contained in sealed quartz tubes under 2.5-3.0 mT vacuum. All samples were heated to 200°C at a ramp rate of 40°C and held there for 12 hours. They were then further heated to 400°C at a ramp rate of 50°C and held for another 12 hours. Finally, they were heated to 900°C at a ramp rate of 50°C and held for a final 12 hours to ensure all components were fully melted. One reaction was cooled at a rate of 5°C/hr to a target temperature of 300°C while the other was cooled at 2°C/hr to see the effects on the crystal growth. Samples were removed from the furnace at 300°C and centrifuged at 3000 rpm for 3 minutes. Samples were finally sonicated in ethanol and acetone to remove quartz wool and flux contaminants.

Although X-Ray Diffraction (XRD) analysis showed ideal chemical composition for Janus Ge_2XY phases, quality single crystals were not obtained. However, there were clear signs of crystal nucleation, particularly for the reaction cooled at 5°C/hr. Abnormal growths on the sides of the quartz tube were found, indicating sublimation during the reaction.

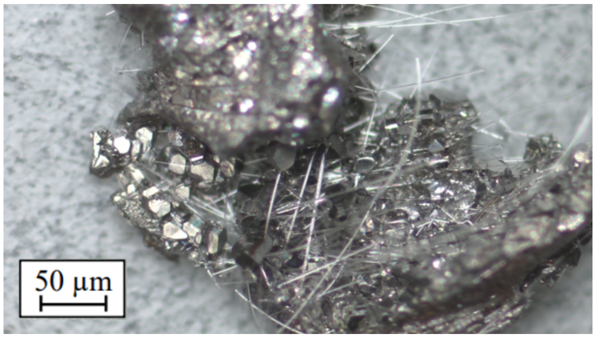


FIG. 1. Flux growth of GexSeyTez with visible signs of nucleation.

III. Results: Chemical Vapor Transport Growths

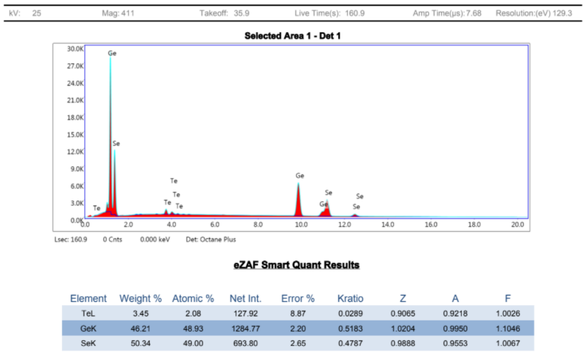
Four experiments were performed with various temperature profiles inside a three zone tube furnace. The raw materials for each sample, and an iodine transport agent, were sealed in quartz tubes under 2.5-3.0 mT vacuum. Often, tubes were tied together with wire and heated in groups of three. The temperature profiles for the reactions were as follows:

1. T_{cold} = 300°C; T_{hot} = 350°C; t = 7 days
2. T_{cold} = 300°C; T_{hot} = 350°C; t = 14 days
3. T_{cold} = 350°C; T_{hot} = 400°C; t = 7 days

4. $T_{cold} = 350°C$; $T_{hot} = 400°C$; t = 14 days

It took seven hours to reach target temperatures in each case. After each reaction, materials were removed and crystals were sonicated with ethanol and acetone to remove any iodine coating.

XRD results for the crystals showed successful single crystal synthesis of pure GeX phases. However, tellurium was notably missing from the composition and binary phases of GeTe were never directly identified. Scanning Electron Microsocopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS) measurements were used to identify surface defects that were composed of iodine and tellurium, indicating the formation of TeI_4.


kV: 25 Mag: 411 Takeoff: 35.9 Live Time(s): 160.9 Amp Time(μs): 7.68 Resolution:(eV) 129.3

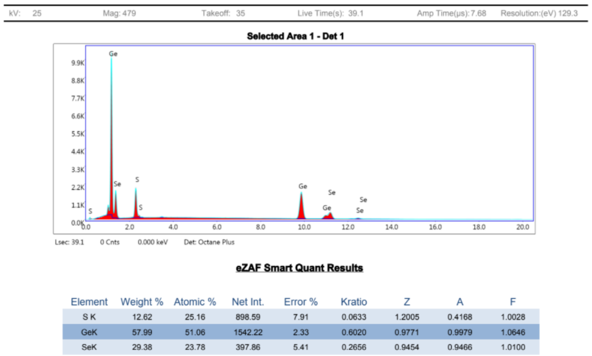
Selected Area 1 - Det 1

Lsec: 160.9 0 Cnts 0.000 keV Det: Octane Plus

eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
TeL	3.45	2.08	127.92	8.87	0.0289	0.9065	0.9218	1.0026
GeK	46.21	48.93	1284.77	2.20	0.5183	1.0204	0.9950	1.1046
SeK	50.34	49.00	693.80	2.65	0.4787	0.9888	0.9553	1.0067

FIG. 2. SEM/EDS data showing low amounts of trace tellurium in a possible GeSe binary crystal.


kV: 25 Mag: 479 Takeoff: 35 Live Time(s): 39.1 Amp Time(μs): 7.68 Resolution:(eV) 129.3

Selected Area 1 - Det 1

Lsec: 39.1 0 Cnts 0.000 keV Det: Octane Plus

eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
S K	12.62	25.16	898.59	7.91	0.0633	1.2005	0.4168	1.0028
GeK	57.99	51.06	1542.22	2.33	0.6020	0.9771	0.9979	1.0646
SeK	29.38	23.78	397.86	5.41	0.2656	0.9454	0.9466	1.0100

FIG. 3. EDS data identifying a possible Janus Ge_2XY crystal.

These results indicate that tellurium doping may be present in the binary phases along with tellurium iodide contamination. Inconsistencies in Single Crystal XRD results support this conclusion. SEM/EDS analysis also identified a potential Janus Ge_2XY composition of Ge_2SSe, as shown in Figure 3. Without further analysis, the crystal composition cannot be confirmed. However, this preliminary analysis is encouraging that Janus Ge_2XY crystal synthesis is possible through CVT methods.

IV. Conclusions

Although the flux growths did not yield the desired single crystals, evidence of nucleation sites indicates this technique could be successful in the future. Most notably, the formation of materials along the quartz tubes during the synthesis process may indicate there was sublimation during the process. This may have affected the reaction in the crucible by limiting the time the crystals could form. So, future attempts may benefit from a lower reaction temperature for a longer time. As for CVT, there can also be improvements made to the synthesis process. Most importantly, another chemical transport should be considered over iodine. Changing the transport agent may lead to more tellurium based GeMC crystals.

V. Future Work

Analysis on the electrical and magnetic properties should be explored using a Physical Property Measurement System (PPMS). Resistivity and hall effect measurements in a PPMS can prove or disprove the appearance of large SOC and PST in these materials. Currently, crystals are in the process of analysis for a temperature dependent resistivity measurement. lastly, further analysis should be conducted to definitively identify the potential Janus Ge_2XY crystal.

VI. Acknowledgements

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[1] M. A. Ulil Absor, Y. Faishal, M. Anshory, I. Santoso, and F. Ishii, Highly persistent spin textures with giant tunable spin splitting in the two-dimensional germanium monochalcogenides, Journal of Physics: Condensed Matter **33**, 305501 (2021).