

University of Alabama in Huntsville

LOUIS

Honors Capstone Projects and Theses

Honors College

4-14-2024

Synthesis and Characterization of Tellurite Based Noncentrosymmetric Materials

Soulathda Monet Le

University of Alabama in Huntsville

Follow this and additional works at: <https://louis.uah.edu/honors-capstones>

Recommended Citation

Le, Soulathda Monet, "Synthesis and Characterization of Tellurite Based Noncentrosymmetric Materials" (2024). *Honors Capstone Projects and Theses*. 899.

<https://louis.uah.edu/honors-capstones/899>

This Thesis is brought to you for free and open access by the Honors College at LOUIS. It has been accepted for inclusion in Honors Capstone Projects and Theses by an authorized administrator of LOUIS.

Synthesis and Characterization of Tellurite-Based Noncentrosymmetric Materials

by

Soulathda Monet Le

An Honors Capstone

submitted in partial fulfillment of the requirements

for the Honors Diploma

to

The Honors College

of

The University of Alabama in Huntsville

Date:

Honors Capstone Project Director: Dr. Jie Ling

Soulathda Monet Le

04/14/2024

Student

Date

Jie Ling

04/01/2024

Project Director

Date

Bernhard Vogler

04/14/2024

Department Chair

Date

Honors College Dean

Date



Honors College

Frank Franz Hall

+1 (256) 824-6450 (voice)

+1 (256) 824-7339 (fax)

honors@uah.edu

Honors Thesis Copyright Permission

This form must be signed by the student and submitted with the final manuscript.

In presenting this thesis in partial fulfillment of the requirements for Honors Diploma or Certificate from The University of Alabama in Huntsville, I agree that the Library of this University shall make it freely available for inspection. I further agree that permission for extensive copying for scholarly purposes may be granted by my advisor or, in his/her absence, by the Chair of the Department, Director of the Program, or the Dean of the Honors College. It is also understood that due recognition shall be given to me and to The University of Alabama in Huntsville in any scholarly use which may be made of any material in this thesis.

Soulathda Monet Le

Student Name (printed)

Soulathda Monet Le

Student Signature

04 / 14 / 2024

Date

Table Of Contents

Abstract	3
Introduction	4
Chapter 1: Material and Methods	6
Chapter 2: Results	8
Chapter 3: Discussion	11
Chapter 4: Conclusion	13
References	14
Images	15
Appendix	22

Abstract

Noncentrosymmetric (NCS) materials have garnered significant attention due to their capacity to display a plethora of technologically important properties, including ferroelectricity, pyroelectricity, piezoelectricity, and second-harmonic generation. An effective approach of producing NCS materials involves introducing cations with inherently asymmetric coordination environment, particularly those containing lone pair cations (i.e., Se 4+, Te 4+, I 5+). In contrast to other lone pair cations like I 5+ and Se 4+, Te 4+ offers a more intricate coordination behavior. In oxide matrices, Te 4+ showcases three distinctive coordination modes: pyramidal TeO₃, seesaw TeO₄, and square pyramidal TeO₅ – all of which possess inherent asymmetry. These Te 4+ oxide polyhedral can subsequently interconnect to forge a diverse array of structures, spanning from discrete clusters to extended one-dimensional chains, two-dimensional sheets, and three-dimensional frameworks. In this study, transition metal oxides or salts were reacted with TeO₂ under hydrothermal conditions to synthesize tellurite compounds.

Introduction

In recent years, noncentrosymmetric (NCS) materials have attracted attention because of their various functional properties. These properties include ferroelectricity, pyroelectricity, piezoelectricity, and nonlinear optical (NLO) properties. These characteristics are essential to industry applications like laser systems, optical communications, photolithography, energy harvesting, detectors, and memories (Ok, 2016). One characteristic of NCS materials that is especially significant to laser technologies is second-harmonic generation (SHG). SHG is a process that induces light frequency doubling and expands a laser's spectrum to cover deep ultraviolet and visible infrared regions (Chen et al., 2021).

SHG is a process that induces light frequency doubling and expands a laser's spectrum to cover deep ultraviolet and visible infrared regions (Chen et al., 2021). An NCS structure is an essential prerequisite for SHG in a crystal. To enhance the polarizability and SHG response of an NCS material, nonbonded lone pair cations like I 5+ and Se 4+ are taken as basic metal ions. Additionally, the Bi 3+ cation has a large polarizability and would have potential for SHG application. If able to crystallize into an NCS structure, combining Bi 3+ and I 5+ or Se 4+ cations can further improve structural diversity and enhance SHG polarizability in NCS materials (Geng et al., 2016).

Combining cations with second order Jahn-Teller distortion, d10 transition metal cations, and anions with trigonal-planar geometry allows several possibilities to obtain NCS structures (Ok, 2016). This experiment mainly focuses on reacting lone pair cations like Se 4+, Te 4+, and I 5+ with transition metal oxides or salts under hydrothermal conditions to form crystals. If NCS

crystals with good SHG polarizability can be successfully synthesized, then those crystal materials would be suitable for laser applications in ultraviolet to mid-infrared bands (Geng et al., 2016).

Chapter 1: Material and Methods

Procedure

In this study, a series of reactions were prepared weekly for 8 weeks. For each reaction, the amount of moles for each reactant was determined based on trial error and previously obtained data. Then by using that amount of moles and the reactant's molar mass, the amount of each reactant in grams was calculated. The amount of reactants for each reaction was measured using an analytical balance. A weigh boat was placed onto the balance and tared to zero. Then the reactant was taken from its source and placed into the weigh boat until the required amount was measured out. This was repeated for each reactant of each reaction. A new weigh boat was used between reactants. The reactions typically had 3 to 4 reactants, so after all reactants for the reaction were measured, all of them were placed into a plastic vial. One plastic vial was used per reaction. Then, 3mL of deionized water was added to the vials. The vials were closed and placed inside a reactor. Once the lids of the reactors were screwed on and secured, they were placed into an oven and heated for 4 days at 200 degrees Celsius. Once the reactions were finished heating, they were left to cool to room temperature and then removed from the oven. The reactors were opened, and the plastic vials were removed. The products in the vials were removed and then isolated using vacuum filtration. As the products were filtrated, they were also washed twice with deionized water and washed twice with an inorganic solution like acetone. Once the product was fully filtrated and dried, it was transferred to a petri dish. The petri dish was then taken and viewed under a microscope to observe for any presence of crystals. Then the plastic vials that contained the products were washed with deionized water and dried. The next week's reactions would then be prepared using those same vials.

Week 1-5 Reactions

During week 1 of the experiment, two reactions were performed. One had SbF_3 , MoO_3 , and I_2O_5 , while the other had SbF_3 , MoO_3 , and SeO_2 . During week 2 of the experiment, two reactions were performed. One was with $\text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4$, MoO_3 , and I_2O_5 and the other was with $\text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4$, MoO_3 , and SeO_2 . Week 3 of the experiment had one reaction with $\text{Bi}(\text{NO}_3)_3$, MoO_3 , and I_2O_5 and another with $\text{Bi}(\text{NO}_3)_3$, MoO_3 , and SeO_2 performed. In week 4 of the experiment, 2 reactions were performed. Both reactions contained $\text{Bi}(\text{NO}_3)_3$, MoO_3 , and SeO_2 . The only difference was that the 2 reactions had different molar ratios for the reactants. Similar to week 4, week 5 of the experiment had 2 reactions, but both reactions contained $\text{Bi}(\text{NO}_3)_3$, MoO_3 , and TeO_2 . The molar ratios were different for each reaction.

Week 6-8 Reactions

Acids and bases were introduced into the reactions in weeks 6 and 7. One reaction from week 6 contained $\text{Bi}(\text{NO}_3)_3$, MoO_3 , TeO_2 , and the acid H_2SO_4 . For this reaction, instead of adding 3 mL of deionized water to the vial, only 2.5 mL of deionized water was added. This was done to accommodate the acid being added to the reaction since H_2SO_4 is a liquid. The second reaction from week 6 contained $\text{Bi}(\text{NO}_3)_3$, MoO_3 , TeO_2 , and the base NaHCO_3 . This reaction was prepared as normal per the procedure. In week 7, one reaction prepared had SbF_3 , MoO_3 , and TeO_2 while the other had SbF_3 , MoO_3 , TeO_2 , and the acid H_2SO_4 . For the reaction with acid, the water added to the vial was once again 2.5 mL to accommodate for the liquid H_2SO_4 that was added. In the last week (week 8), the reactions prepared had $\text{Bi}(\text{NO}_3)_3$, V_2O_5 , and SeO_2 , and the other had $\text{Bi}(\text{NO}_3)_3$, V_2O_5 , and TeO_2 .

Chapter 2: Results

In week 1 of the experiment, the ratio of mmol for SbF_3 , MoO_3 , and I_2O_5 in reaction 1 and for SbF_3 , MoO_3 , and SeO_2 in reaction 2 was both 1:1:2. This ratio was decided as a starting point. Both reactions produced white powder with no crystals present. Since no crystals were produced in week 1's reactions, week 2 replaced SbF_3 with $\text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4$ since both Sb^{3+} and Bi^{3+} are ions that can have an octahedral coordination. The mmol ratio for $\text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4$, MoO_3 , and I_2O_5 in reaction 1 and $\text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4$, MoO_3 , and SeO_2 in reaction 2 were both $\frac{1}{2}$:1:2. This ratio was decided just as a trial. Reaction 1 of week 2 produced white powder with no crystals. Reaction 2 of week 2 produced white powder with some colorless crystals present. An example of the products from Week 1 and Reaction 1 of Week 2 is shown in Image 1. The product of reaction 2 from week 2 is shown in Image 2. In week 3, $\text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4$ was replaced with $\text{Bi}(\text{NO}_3)_3$ to see if a different salt with Bi^{3+} would produce more crystals. The mmol ratio for $\text{Bi}(\text{NO}_3)_3$, MoO_3 , and I_2O_5 in reaction 1 for $\text{Bi}(\text{NO}_3)_3$, MoO_3 , and SeO_2 in reaction 2 was both 1:1:2. Since the presence of Bi^{3+} produced crystals, the amount of Bi^{3+} was increased for week 3 reactions and the amounts of the lone pair cations (I^{5+} and Se^{4+}) and MoO_3 were kept constant as a control of sorts. Reaction 1 of week 3 produced white powder with some tiny needle-shaped crystals, which can be viewed in Image 3. Reaction 2 of week 3 produced white powder with some prism-shaped crystals, which can be viewed in Image 4.

Week 4 of the experiment contained two different reactions of $\text{Bi}(\text{NO}_3)_3$, MoO_3 , and SeO_2 . Reaction 1 had the mmol ratio of the reactants at 2:1:4, while reaction 2 had a mmol ratio of 1:2:4. The different ratios of the same reaction were done to see whether more Bi^{3+} or more d10 transition metal (Mo^{6+}) would produce more crystals. The amount of Se^{4+} was increased

as a trial and kept constant between the reactions. Reaction 1 of week 4 produced white powder with few crystals while reaction 2 produced white powder with prism shaped crystals. The products for reactions 1 and 2 of week 4 can be viewed in Images 5 and 6, respectively. In week 5, SeO_2 was replaced with TeO_2 to trial a different lone pair cation. There were two different reactions of $\text{Bi}(\text{NO}_3)_3$, MoO_3 , and TeO_2 . Reaction 1 had a mmol ratio of 2:1:4, while reaction 2 had a mmol ratio of 1:2:4. The difference in ratios was to test the effect of more Bi^{3+} on crystal production when Te^{4+} is used as the lone pair cation. Reaction 1 produced a yellowish powder with some needle-shaped crystals, while reaction 2 produced a yellowish powder with no crystals. The products for reactions 1 and 2 of week 5 can be viewed in Images 7 and 8, respectively.

In weeks 6 and 7 of the experiment, acids and bases were introduced to the reactions. In week 6, reaction 1 had $\text{Bi}(\text{NO}_3)_3$, MoO_3 , TeO_2 , and the acid H_2SO_4 ; however, reaction 2 had $\text{Bi}(\text{NO}_3)_3$, MoO_3 , TeO_2 , and the base NaHCO_3 . Both reactions had a mmol ratio of 2:1:4:1. These reactions were completed to compare the effects of acids and bases on crystal production. Reaction 1 produced white powder with colorless crystals, which can be seen in Image 9. Reaction 2 produced white and yellow powder, which can be seen in Image 10. In week 7, reaction 1 had SbF_3 , MoO_3 , and TeO_2 , while reaction 2 had SbF_3 , MoO_3 , TeO_2 , and the acid H_2SO_4 . Reaction 1 had a mmol ratio of 2:1:4, while reaction 2 had a mmol ratio of 2:1:4:1. Since the addition of acid seemed to have a positive effect on crystal production in week 6, this set of reactions was done to compare the effect of acids on crystal production versus having no acid at all. Reaction 1 produced mostly powder but contained very tiny crystals. Reaction 2 produced yellow powder with some colorless crystals. The products of reactions 1 and 2 for week 7 can be seen in Images 11 and 12, respectively.

In week 8 of the experiment, MoO₃ was replaced with V₂O₅ to trial a different d10 transition metal. Reaction 1 contained Bi(NO₃)₃, V₂O₅, and SeO₂ and reaction 2 contained Bi(NO₃)₃, V₂O₅, and TeO₂. Both reactions had a mmol ratio of 1:1:2. Since this set of reactions trialed a different d10 transitional metal, two different reactions with Se 4+ and Te 4+ were completed to compare the effect on crystal production. Both reactions 1 and 2 produced orange powder with no crystals, which can be viewed in Images 13 and 14, respectively.

Chapter 3: Discussion

It was found that when a reaction contained Bi^{3+} , the reaction was more likely to produce crystals than the reactions without Bi^{3+} . When $\text{Bi}(\text{NO}_3)_3$ was used instead of $\text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4$, the reactions produced more crystals. When both reactions in a week contained different amounts of Bi^{3+} , it is unclear whether more or less Bi^{3+} produced more crystals. When a reaction had more Bi^{3+} present than the other in Week 4, the reaction that contained more Bi^{3+} had fewer amount of crystals formed than the reaction that had less Bi^{3+} . In Week 5, the reaction that had more Bi^{3+} present produced more crystals than the reaction with less Bi^{3+} . Therefore, further investigation into different ratios of reactants and the effects of different quantities of Bi^{3+} on crystal production would need to be conducted before a clear conclusion can be made.

When comparing the different reactions that contained I^{5+} , Se^{4+} , or Te^{4+} , the reactions that contained Se^{4+} and Te^{4+} were more likely to produce more crystals than with I^{5+} . When Se^{4+} was reacted with Sb^{3+} like in reaction 2 of week 1, no crystals were produced. However, when Te^{4+} was reacted with Sb^{3+} like in reaction 1 of week 7, crystals were produced. Therefore, it can be concluded that Te^{4+} has a higher likelihood of producing more crystals when reacted with Sb^{4+} than Se^{4+} . When Mo^{6+} was used as the d10 transition metal in the reactions, Se^{4+} and Te^{4+} produced crystals. However, when Mo^{6+} was switched out for V^{5+} , both Se^{4+} and Te^{4+} produced no crystals. Therefore, Se^{4+} and Te^{4+} have a higher likelihood of producing crystals when reacted with Mo^{6+} instead of V^{5+} .

For the reactions that had either an acid or a base added to it, the reaction with an acid added produced more crystals than the reaction with a base. When comparing a reaction with acid to a reaction with no acid present, the reaction with acid produced more crystals. Therefore,

the addition of an acid had a positive effect on the production of crystals. Further research could be done to determine if the strength of acid affects the production of crystals.

Chapter 4: Conclusion

Overall, crystals were mostly produced when Bi^{3+} was present in the reaction. However, it is unclear whether a greater amount or lesser amount of Bi^{3+} in the reaction would produce more crystals. Therefore, more trials related to this effect would need to be conducted. Crystals were mostly produced when the reactions had Se^{4+} or Te^{4+} . However, when reacted with Mo^{6+} , the reaction produced more crystals than with V^{5+} . For reactions with acid or base added, acid had a positive effect on crystal production. Additionally, there were still different trials that could have been performed but were not included in this experiment. For example, there could be changes in temperature, heating duration, water amount, different reactant ratios, strength of acid or base, etc. that could affect the production of crystals. Therefore, more research about efficient methods of tellurite crystal production would need to be conducted for a firmer conclusion.

References

- Chen, J.; Hu, C.-L.; Kong, F.; Mao, J.-G. High-Performance Second Harmonic-Generation (SHG) Materials: New Developments and New Strategies. *Accounts of Chemical Research* **2021**, *54* (12), 2775–2783. DOI: 10.1021/acs.accounts.1c00188.
- Geng, L.; Li, W.; Zhu, B.; Ma, S.; Liu, B.; Jiang, K.; Lu, H.; Meng, C. Polar Bismuth Selenite Iodate Oxide BiSeIO₆ with Three Types of Lone Pair Cations in One Structure. *Inorganic Chemistry* **2023**, *62* (6), 2887–2893. DOI: 10.1021/acs.inorgchem.2c04323.
- Ok, K. M. Toward the Rational Design of Novel Noncentrosymmetric Materials: Factors Influencing the Framework Structures. *Accounts of Chemical Research* **2016**, *49* (12), 2774–2785. DOI: 10.1021/acs.accounts.6b00452.

Images

Image 1: Product of Reactions 1 and 2 of Week 1 and Reaction 1 of Week 2

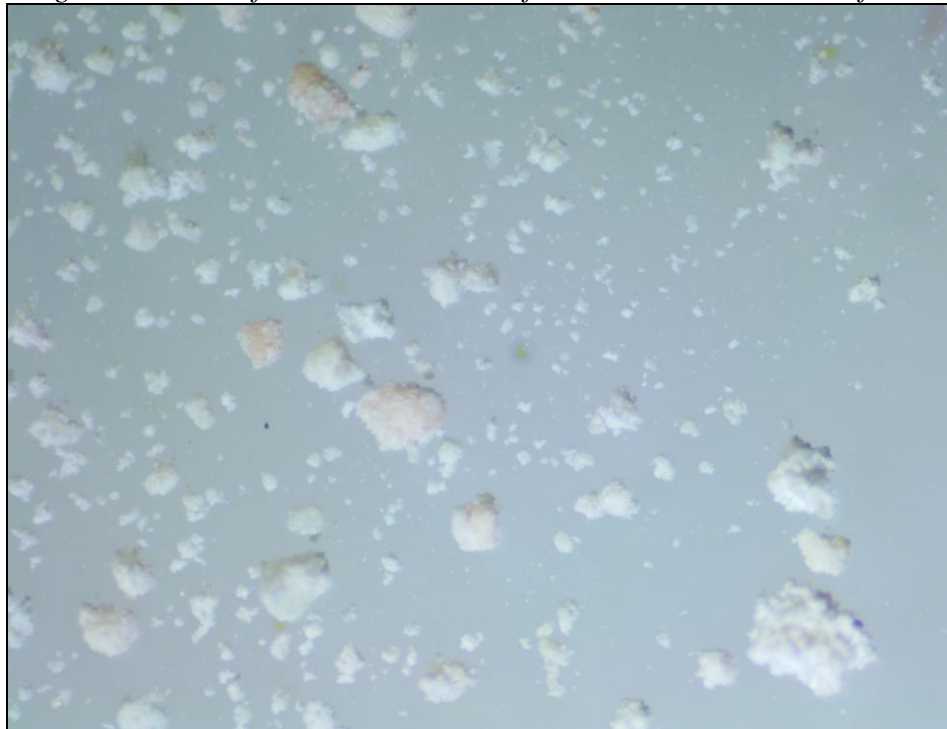
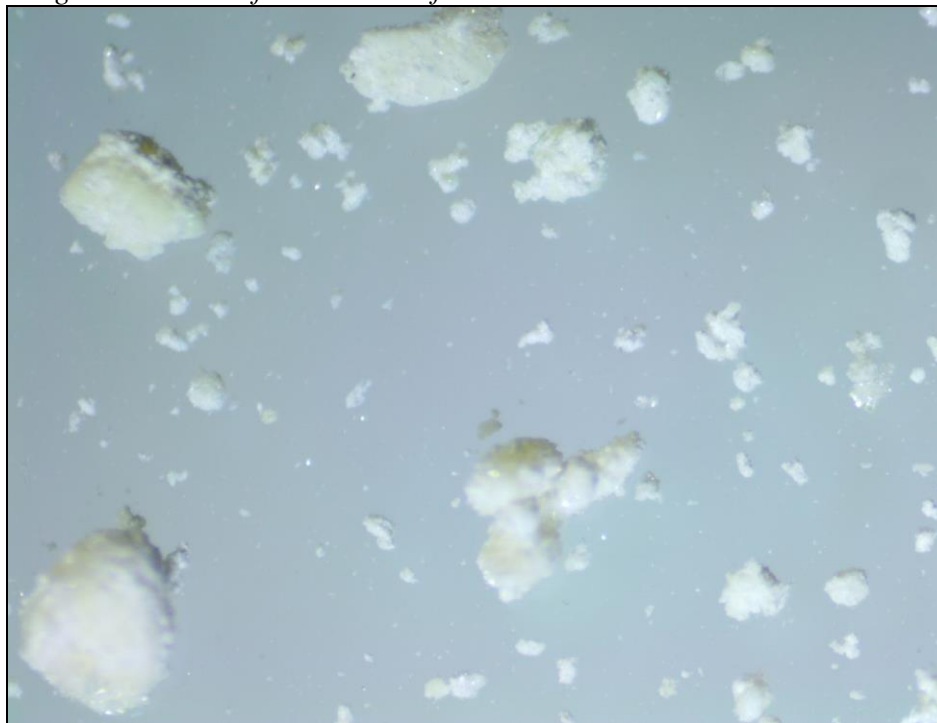


Image 2: Product of Reaction 2 of Week 2



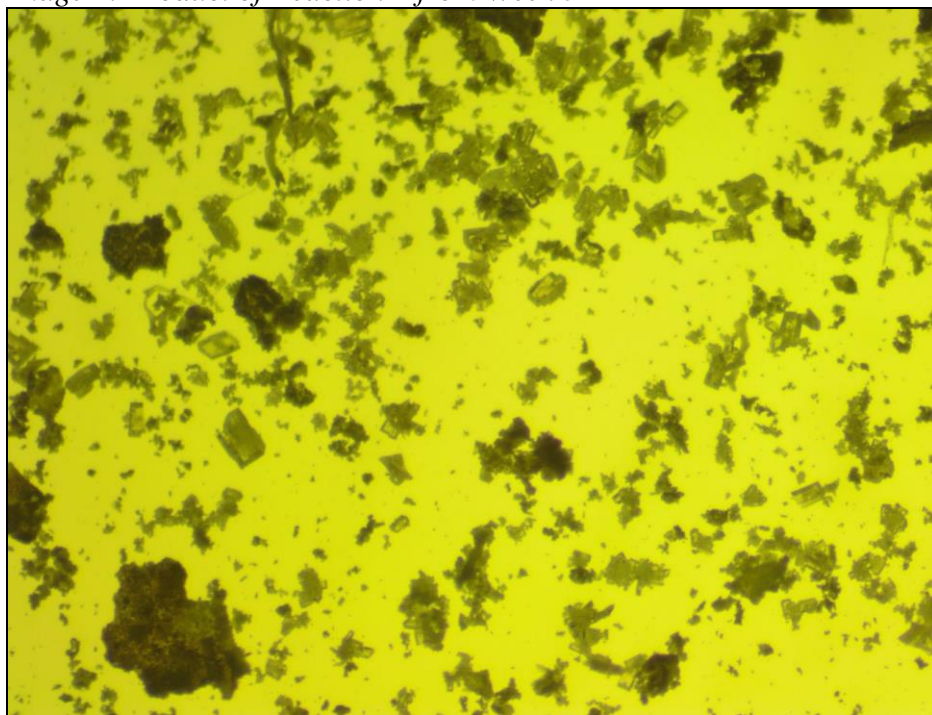
The small shiny particles indicate the presence of crystals.

Image 3: Product of Reaction 1 from Week 3



The small shiny particles signify the presence of crystals.

Image 4: Product of Reaction 2 from Week 3



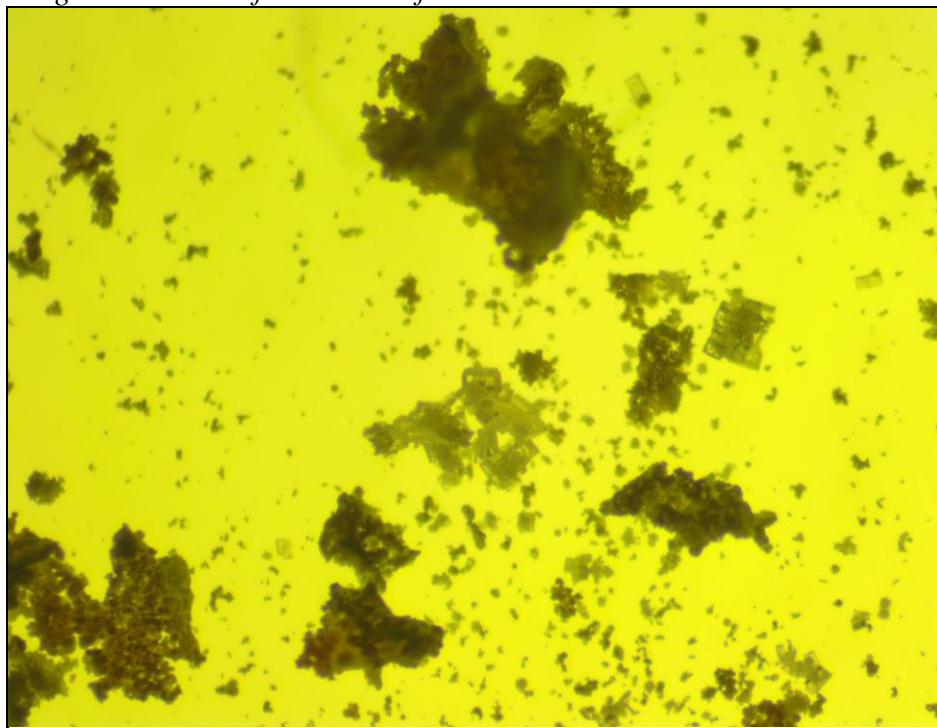
The block-looking particles are the presence of crystals, which shows the shape of the crystals clearly.

Image 5: Product of Reaction 1 from Week 4



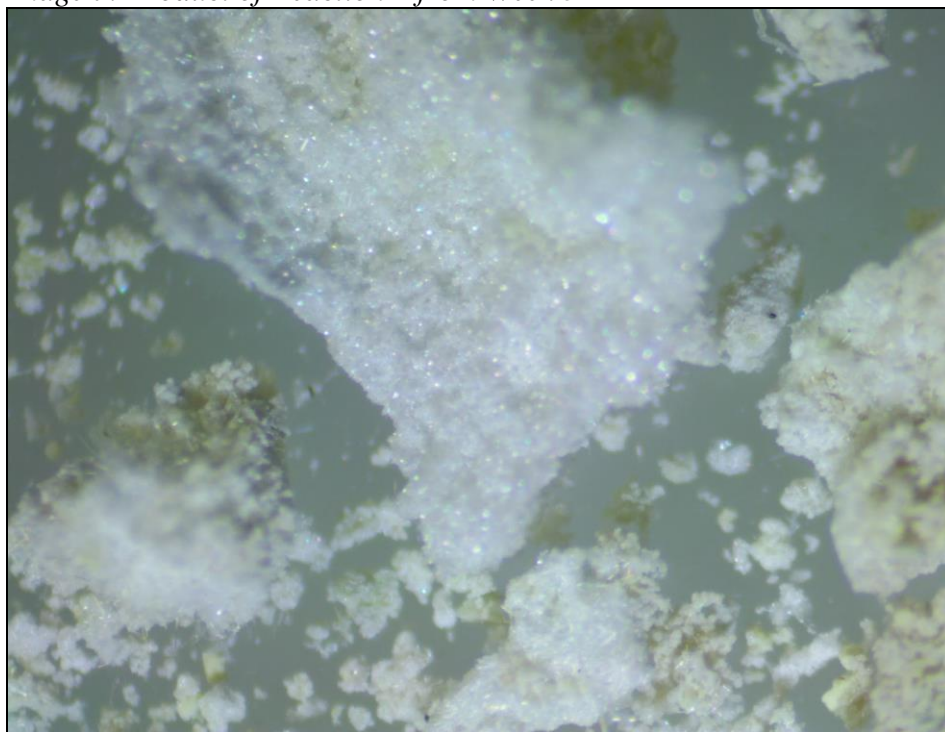
The small shiny particles signify the presence of crystals.

Image 6: Product of Reaction 2 from Week 4



The block-looking particles are the presence of crystals, which shows the shape of the crystals clearly.

Image 7: Product of Reaction 1 from Week 5



The small shiny particles indicate the presence of crystals.

Image 8: Product of Reaction 2 from Week 5

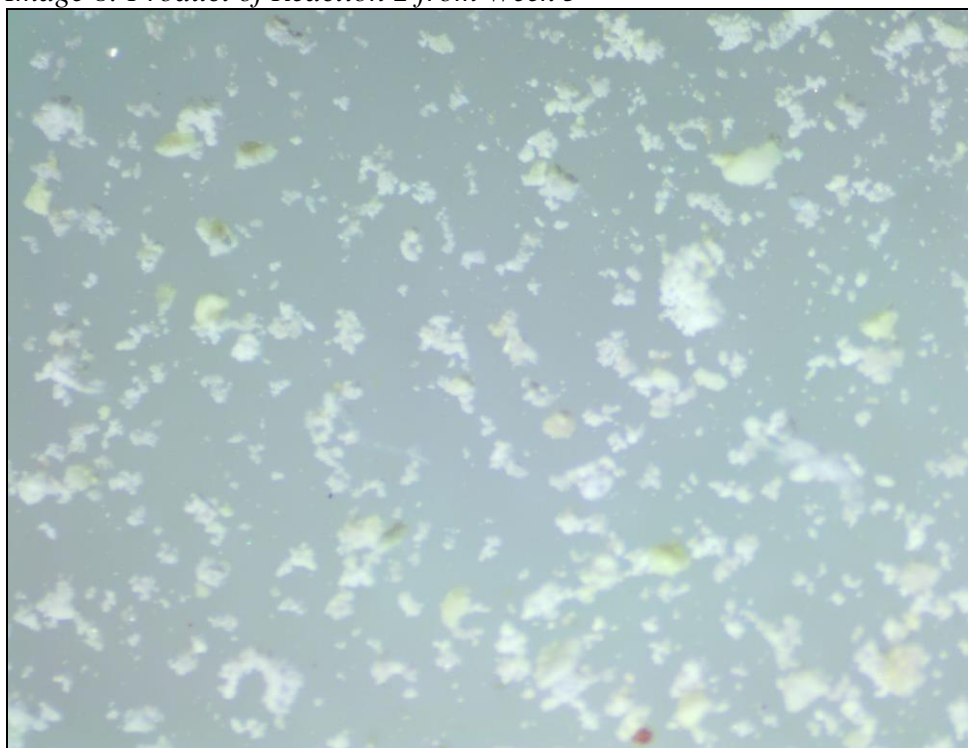
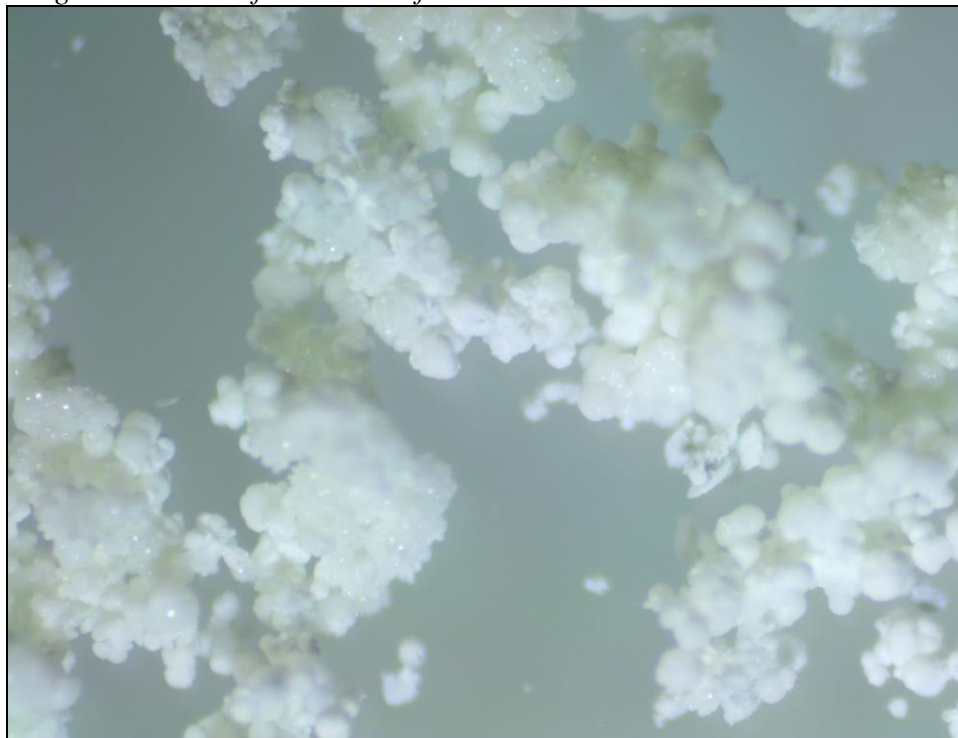


Image 9: Product of Reaction 1 from Week 6



The small shiny particles indicate the presence of crystals.

Image 10: Product of Reaction 2 from Week 6

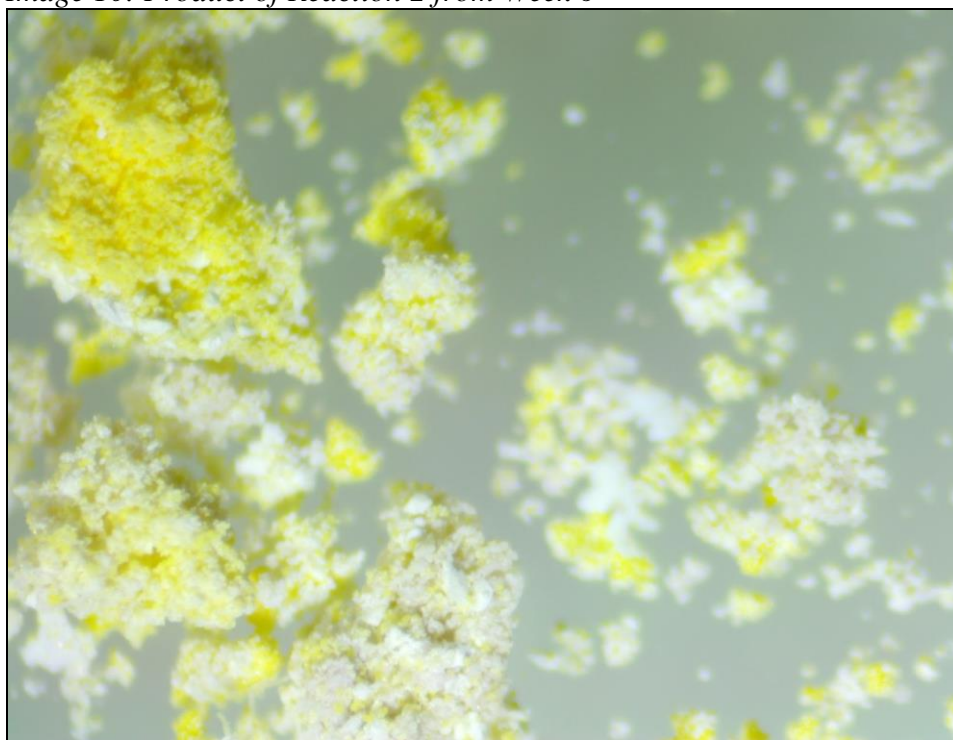
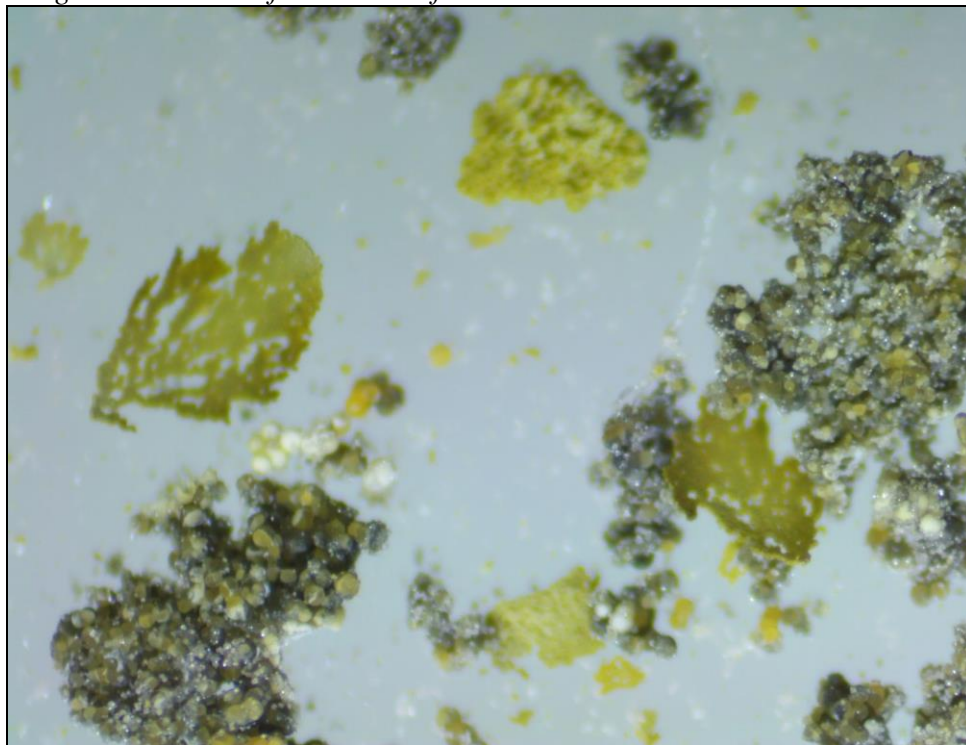
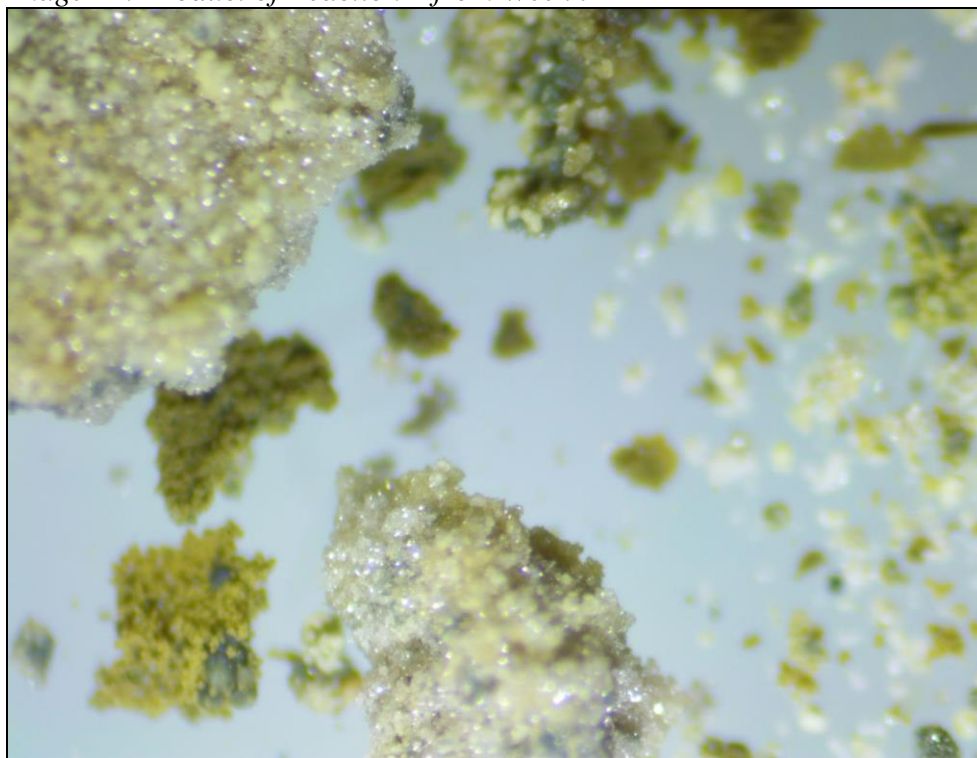


Image 11: Product of Reaction 1 from Week 7



The small shiny particles indicate the presence of crystals.

Image 12: Product of Reaction 2 from Week 7



The small shiny particles indicate the presence of crystals.

Image 13: Product of Reaction 1 from Week 8

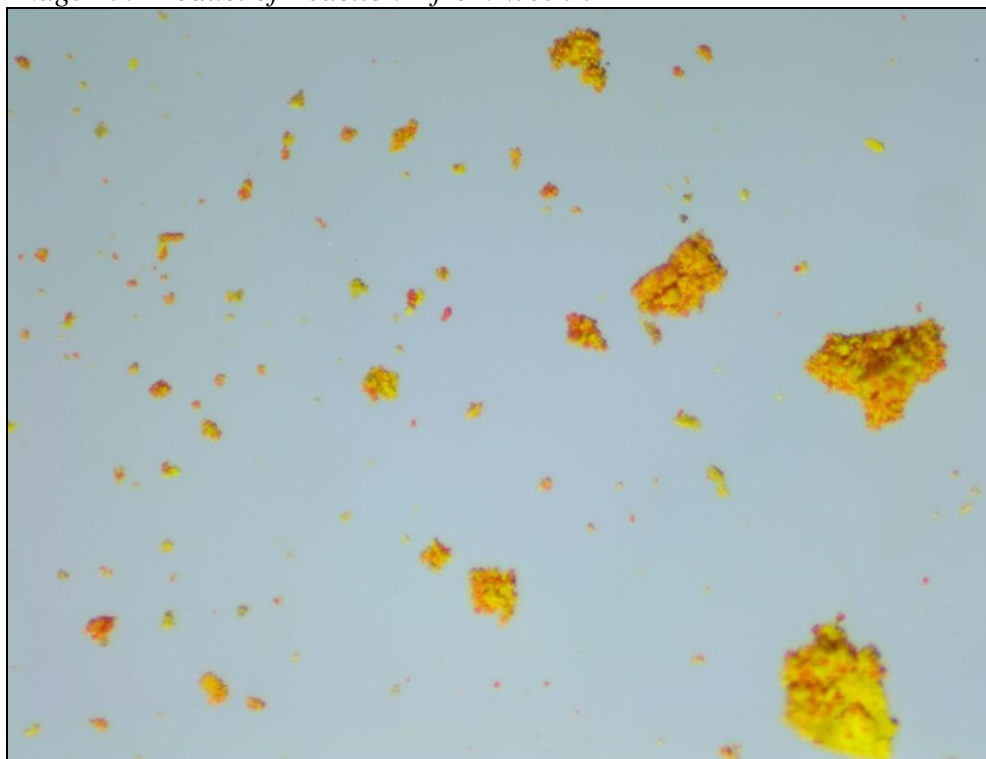
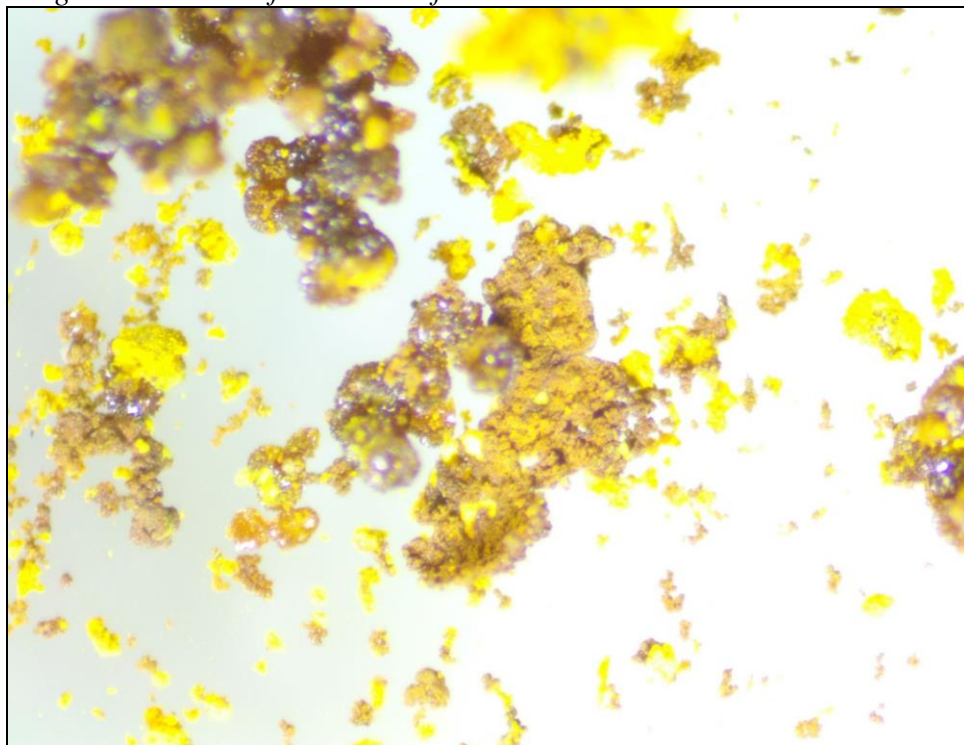


Image 14: Product of Reaction 2 from Week 8



Appendix

Table 1: Raw Data of the Reactions in the Experiment

Week #	Reaction	Mass of Reactants, in respective order (g)	Ratio of Reactants	Product
1	SbF ₃ , MoO ₃ , and I ₂ O ₅	0.045, 0.036, 0.167	1:1:2	White powder
	SbF ₃ , MoO ₃ , and SeO ₂	0.045, 0.036, 0.055	1:1:2	White powder
2	Bi ₅ O(OH) ₉ (NO ₃) ₄ , MoO ₃ , and I ₂ O ₅	0.0731, 0.036, 0.167	1/5 :1:2	White powder
	Bi ₅ O(OH) ₉ (NO ₃) ₄ , MoO ₃ , and SeO ₂	0.0731, 0.036, 0.055	1/5 :1:2	White powder with some colorless crystals
3	Bi(NO ₃) ₃ , MoO ₃ , and I ₂ O ₅	0.121, 0.036, 0.167	1:1:2	White powder with maybe tiny needle shaped crystals
	Bi(NO ₃) ₃ , MoO ₃ , and SeO ₂	0.121, 0.036, 0.055	1:1:2	White powder with some □ shaped crystal
4	Bi(NO ₃) ₃ , MoO ₃ , and SeO ₂	0.242, 0.036, 0.111	2:1:4	White powder with little amount of crystals
	Bi(NO ₃) ₃ , MoO ₃ , and SeO ₂	0.121, 0.072, 0.111	1:2:4	White powder with some crystals
5	Bi(NO ₃) ₃ , MoO ₃ , and TeO ₂	0.242, 0.036, 0.160	2:1:4	Powder with some needle-shaped crystals

	Bi(NO ₃) ₃ , MoO ₃ , and TeO ₂	0.121, 0.072, 0.160	1:2:4	Powder and no crystals
6	Bi(NO ₃) ₃ , MoO ₃ , TeO ₂ , and H ₂ SO ₄	0.242, 0.036, 0.160, 0.5 mL	2:1:4:1	White powder with colorless crystal
	Bi(NO ₃) ₃ , MoO ₃ , TeO ₂ , and NaHCO ₃	0.242, 0.036, 0.160, 0.0210	2:1:4:1	White and yellow powder
7	SbF ₃ , MoO ₃ , and TeO ₂	0.09, 0.036, 0.160	2:1:4	Mostly powder but very tiny crystals
	SbF ₃ , MoO ₃ , TeO ₂ , and H ₂ SO ₄	0.09, 0.036, 0.160, 0.5 mL	2:1:4:1	Some colorless crystals
8	Bi(NO ₃) ₃ , V ₂ O ₅ , and SeO ₂	0.121, 0.045, 0.055	1:1:2	Orange powder
	Bi(NO ₃) ₃ , V ₂ O ₅ , and TeO ₂	0.121, 0.045, 0.079	1:1:2	Orange powder