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Synthesis and Characterization of Tellurite Based Noncentrosymmetric Materials

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Synthesis and Characterization of Tellurite Based Noncentrosymmetric Materials

by

Jackson Price Jones

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Jackson Jones

Student Name (printed)

Jackson Jones

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04/29/2024

Date

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Abstract

Noncentrosymmetric materials are crystals without a symmetric center. They exhibit many important characteristics, including second-harmonic generation, piezoelectricity, and birefringence. In this experiment, 23 hydrothermal reactions were conducted over the course of a semester to synthesize novel noncentrosymmetric materials. In these reactions, reagents, molar ratios, temperatures of reaction, and time of reaction were varied. Of the 23 reactions, 1 did not produce any solid product, 5 produced powders, and the other 17 produced crystals. In the future, more analysis would need to be done on these crystals to determine their composition, purity, and characteristics. Additionally, more variation could be always done on the conditions of synthesis for novel materials.

Introduction

Noncentrosymmetric structures are crystals that do not have an inversion center. They have several important properties to their applications in lasers, batteries, and electronics. These properties include piezoelectricity, pyroelectricity, and ferroelectricity as well as second-harmonic generation.[1] Piezoelectricity describes the ability of a material to convert mechanical energy to electrical energy. Pyroelectricity is the change in polarization as temperature changes. Ferroelectric materials are pyroelectric materials whose polarization can be reversed when voltage is applied to the material. Second-harmonic generation (SHG) occurs when 2 photons that have the same energy interact with a noncentrosymmertric material. The two photons combine into one, which doubles the energy and therefore the frequency, while halving the wavelength. This is one way in which noncentrosymmetric materials can be compared to one another, generally by comparing the output of any material to the output of a standard.[2] Additionally, noncentrosymmetric materials are often the same materials as nonlinear optical materials, and they share many properties.[1]

For a material to be nonlinearly optical, it must meet several criteria. First, it must crystallize in a noncentrosymmetric space group. Second, it must have a significant second harmonic generation, though there is no universal established value applicable to all materials. Third, it must have a high laser damage threshold. This is how much of a laser at a specific energy and power per area a material can take before it is damaged irreversibly by the laser. Fourth, the material must have a large enough birefringence to properly phase-match. This means that the birefringence generally increases as the harmonic wavelength for SHG decreases.[3] Birefringence refers to splitting a beam into two polarized perpendicular beams; it is a property exhibited by anisotropic crystals.[4] Fifth, the material must be stable and easy to synthesize, at least for practical purposes.[3]

Noncentrosymmetric materials can be classified by the region of light in which they are transparent: IR, near IR and visible, and UV. Within each of these categories, there are generally certain classes of materials that make up the category. Within IR, many of the materials can be classified as metal chalcogenides and, to a lesser extent, metal pnictides. Within the near IR and visible category, the classes include metal phosphates and metal iodates. Within the UV category, the classes include metal borates, metal carbonates and nitrates, metal antimonies and metal phosphates. Additionally, different building blocks can be combined to create more variety of noncentrosymmetric groups, such as metal borophosphates.[3,5]

Noncentrosymmetric materials are often formed through solid-state hydrothermal reactions.[3] Several asymmetric building blocks are often used in an attempt to make noncentrosymmetric materials. These include d^0 transition metal cations which are octahedrally coordinated, which may undergo second-order Jahn-Teller distortions. These cations include V^{5+}, Mo^{6+}, and Ti^{4+}, among others. Along with these cations, cations with “stereochemically active lone pairs,” including Te^{4+}, Se^{4+}, and I^{5+} are used.[1] Particularly of note is that Te^{4+} can form three different geometries, allowing for more different forms to be used in a noncentrosymmetric material. Building blocks may also include d^{10} transition metal cations like Zn^{2+} and Cd^{2+}. Anions that have trigonal planar geometry can also be building blocks for noncentrosymmetric materials.[1] While the use of these asymmetric building blocks does not guarantee a noncentrosymmetric material will be synthesized under all conditions, using asymmetric groups does increase this likelihood.

Fluorination is a tactic that is often used to replace some oxygen atoms within a material with fluorine atoms. These fluorine atoms can be coordinated with either the d^0 transition metal cation or with the other cations present within a material.[6] This will change the coordination environment around a metal atom due to the difference in electronegativity and size between oxygen and fluorine atoms, which can affect the crystallization of the material. Additionally, adding another atom allows for more possibilities of asymmetric groups forming as new materials are synthesized. Fluorination allows for the synthesis of more new materials, and it also changes the properties of the materials that are synthesized, when compared to the similar, nonfluorinated materials. For example, the presence of fluorine atoms within a material may change its second-harmonic generation values, largely depending on the specific material and its structure. Additionally, the band gap, UV cutoff, and birefringence can also be changed when a material is fluorinated.[7] However, fluorination of the material is difficult to control. Partial fluorination can be difficult to obtain, while no fluorination or complete fluorination may occur incidentally with the addition of too little or too much fluorine, respectively, to the reaction.[8]

Materials and Methods

23 hydrothermal reactions were prepared over the course of the semester. Reagents used in these reactions were already available in the lab of the supervisor. Reagents were used as stored, without further purification. The reagents used, their molar ratios, the temperature of the oven, and the time of the reaction were varied in an attempt to synthesize different materials, based on prior experiments. Conditions and reagents for reactions that were completed are described in the Reactions subsection.

Metal hydrothermal synthesis autoclaves and Teflon reaction vessels were used for the reactions. The determined amount of each reagent was calculated based on the molar mass of the reagent and the desired molar ratio of reagents. The desired mass of each reagent was measured using an analytical balance. After measuring, reagents were added to the Teflon reaction vessels. Then the determined amount of water was added, using a micropipette, followed by the determined amount of hydrofluoric acid, also added using a micropipette. Once the reactants were placed into the reaction vessels and the reaction vessels were closed, the reaction vessels were placed into the metal hydrothermal synthesis autoclaves. The autoclaves were reassembled, and the lid was screwed on. The autoclaves were then placed into the oven, which was heated, and the reaction was allowed to continue for several days. After the reaction was complete, the oven cooled, and the autoclaves were removed from the oven. The reaction vessels were removed from the autoclaves, and they were opened. Observations were made about the contents of the reaction vessels – whether they contained liquid and the color of any liquid or solid within the reaction vessel.

A vacuum filtration system was set up. The vacuum was created using a water aspirator, and it was connected to a side-arm flask. The filter was composed of filter paper within a Buchner funnel. After the reaction vessel was opened, the contents were poured onto the filter paper, and they were rinsed thoroughly, first with distilled water, then with acetone. Once the product was filtered, the filter paper was removed from the funnel and the crystals or powder were poured and scraped into a labelled petri dish. Synthesized products were stored in small petri dishes labelled with experimenter initials, date of synthesis, and the number of the reaction. These numbers did not correspond to the numbers used in the Reactions section, but rather to the number of the autoclave used in the reaction. After filtration, reaction vessels and all tools used were cleaned using water and acetone, and products were observed under a light microscope.

Reactions

1. $BaF_2 + MoO_3 + TeO_2 + HF$ at 220°C for 4 days with 1mL of water

In this reaction, 0.088g (0.5mmol) BaF_2, 0.072g (0.5mmol) MoO_3, and 0.08g (0.5mmol) TeO_2 were added to the reaction vessel. 1mL of water was added, then 0.25mL of HF was added. This reaction occurred for 4 days at 220°C.

2. $BaF_2 + 2MoO_3 + TeO_2 + HF$ at 220°C for 4 days with 1mL of water

In this reaction, 0.088g (0.5mmol) BaF_2, 0.144g (1mmol) MoO_3, and 0.08g (0.5mmol) TeO_2 were added to the reaction vessel. 1mL of water was added, then 0.25mL of HF was added. This reaction occurred for 4 days at 220°C.

3. $BaF_2 + TeO_2 + HF$ at 220°C for 4 days with 1mL of water

In this reaction, 0.088g (0.5mmol) BaF_2 and 0.08g (0.5mmol) TeO_2 were added to the reaction vessel. 1mL of water was added, then 0.25mL of HF was added. This reaction occurred for 4 days at 220°C.

4. $Na_2CO_3 + TeO_2 + HF$ at 220°C for 4 days with 1mL of water

In this reaction, 0.053g (0.5mmol) Na_2CO_3 and 0.08g (0.5mmol) TeO_2 were added to the reaction vessel. 1mL of water was added, then 0.25mL of HF was added. This reaction occurred for 4 days at 220°C.

5. $BaF_2 + MoO_3 + TeO_2 + HF$ at 220°C for 4 days with 1mL of water

In this reaction, 0.088g (0.5mmol) BaF_2, 0.072g (0.5mmol) MoO_3, and 0.08g (0.5mmol) TeO_2 were added to the reaction vessel. 1mL of water was added, then 0.25mL of HF was added. This reaction occurred for 4 days at 220°C. This reaction was done as a repeat of reaction 1.

6. $BaF_2 + TeO_2 + HF$ at 220°C for 4 days with 1mL of water

In this reaction, 0.088g (0.5mmol) BaF_2 and 0.08g (0.5mmol) TeO_2 were added to the reaction vessel. 1mL of water was added, then 0.25mL of HF was added. This reaction occurred for 4 days at 220°C. This reaction was done as a repeat of reaction 3.

7. $4BaF_2 + V_2O_5 + 2I_2O_5 + HF$ at 200°C for 3 days with 4mL of water

In this reaction, 0.088g (0.5mmol) BaF_2, 0.023g (0.125mmol) V_2O_5, and 0.084g (0.25mmol) I_2O_5 were added to the reaction vessel. 4mL of water was added, then 0.3mL of HF was added. This reaction occurred for 3 days at 200°C.

8. $2BaF_2 + 2MoO_3 + I_2O_5 + HF$ at 200°C for 3 days with 4mL of water

In this reaction, 0.088g (0.5mmol) BaF_2, 0.072g (0.5mmol) MoO_3, and 0.084g (0.25mmol) I_2O_5 were added to the reaction vessel. 4mL of water was added, then 0.3mL of HF was added. This reaction occurred for 3 days at 200°C.

9. $BaF_2 + MoO_3 + TeO_2 + HF$ at 220°C for 4 days with 4 mL of water

In this reaction, 0.088g (0.5mmol) BaF_2, 0.072g (0.5mmol) MoO_3, and 0.08g (0.5mmol) TeO_2 were added to the reaction vessel. 4mL of water was added, then 0.1mL of HF was added. This reaction occurred for 4 days at 220°C.

10. $BaF_2 + MoO_3 + TeO_2 + HF$ at 220°C for 4 days with 4 mL of water

In this reaction, 0.088g (0.5mmol) BaF_2, 0.072g (0.5mmol) MoO_3, and 0.08g (0.5mmol) TeO_2 were added to the reaction vessel. 4mL of water was added, then 0.25mL of HF was added. This reaction occurred for 4 days at 220°C.

11. $BaF_2 + MoO_3 + TeO_2 + HF$ at 220°C for 4 days with 4 mL of water

In this reaction, 0.088g (0.5mmol) BaF_2, 0.072g (0.5mmol) MoO_3, and 0.08g (0.5mmol) TeO_2 were added to the reaction vessel. 4mL of water was added, then 0.5mL of HF was added. This reaction occurred for 4 days at 220°C.

12. $4BaF_2 + V_2O_5 + 2I_2O_5 + HF$ at 230°C for 4 days with 4mL of water

In this reaction, 0.088g (0.5mmol) BaF_2, 0.023g (0.125mmol) V_2O_5, and 0.084g (0.25mmol) I_2O_5 were added to the reaction vessel. 4mL of water was added, then 0.3mL of HF was added. This reaction occurred for 4 days at 230°C.

13. $2BaF_2 + 2MoO_3 + I_2O_5 + HF$ at 230°C for 4 days with 4mL of water

In this reaction, 0.088g (0.5mmol) BaF_2, 0.072g (0.5mmol) MoO_3, and 0.084g (0.25mmol) I_2O_5 were added to the reaction vessel. 4mL of water was added, then 0.2mL of HF was added. This reaction occurred for 4 days at 230°C.

14. $2BaF_2 + 2MoO_3 + I_2O_5 + HF$ at 230°C for 4 days with 4mL of water

In this reaction, 0.088g (0.5mmol) BaF_2, 0.072g (0.5mmol) MoO_3, and 0.084g (0.25mmol) I_2O_5 were added to the reaction vessel. 4mL of water was added, then 0.4mL of HF was added. This reaction occurred for 4 days at 230°C.

15. $4BaF_2 + V_2O_5 + 2I_2O_5 + HF$ at 230°C for 4 days with 4mL of water

In this reaction, 0.088g (0.5mmol) BaF_2, 0.023g (0.125mmol) V_2O_5, and 0.084g (0.25mmol) I_2O_5 were added to the reaction vessel. 4mL of water was added, then 0.15mL of HF was added. This reaction occurred for 4 days at 230°C.

16. $4BaF_2 + 4MoO_3 + I_2O_5 + HF$ at 230°C for 4 days with 4mL of water

In this reaction, 0.088g (0.5mmol) BaF_2, 0.072g (0.5mmol) MoO_3, and 0.042g (0.125mmol) I_2O_5 were added to the reaction vessel. 4mL of water was added, then 0.15mL of HF was added. This reaction occurred for 4 days at 230°C.

17. $8NaF + 4MoO_3 + I_2O_5 + HF$ at 230°C for 4 days with 4mL of water

In this reaction, 0.042g (1mmol) NaF, 0.072g (0.5mmol) MoO_3, and 0.042g (0.125mmol) I_2O_5 were added to the reaction vessel. 4mL of water was added, then 0.15mL of HF was added. This reaction occurred for 4 days at 230°C.

18. $4BaF_2 + V_2O_5 + 2I_2O_5 + HF$ at 230°C for 4 days with 4mL of water

In this reaction, 0.088g (0.5mmol) BaF_2, 0.023g (0.125mmol) V_2O_5, and 0.084g (0.25mmol) I_2O_5 were added to the reaction vessel. 4mL of water was added, then 0.3mL of HF was added. This reaction occurred for 4 days at 230°C. This reaction was done as a repeat of reaction 12.

19. $4MgF_2 + 4MoO_3 + I_2O_5 + HF$ at 230°C for 4 days with 4mL of water

In this reaction, 0.031g (0.5mmol) MgF_2, 0.072g (0.5mmol) MoO_3, and 0.042g (0.125mmol) I_2O_5 were added to the reaction vessel. 4mL of water was added, then 0.3mL of HF was added. This reaction occurred for 4 days at 230°C.

20. $2CdCO_3 + 2MoO_3 + I_2O_5 + HF$ at 230°C for 4 days with 4mL of water

In this reaction, 0.086g (0.5mmol) $CdCO_3$, 0.072g (0.5mmol) MoO_3, and 0.084g (0.25mmol) I_2O_5 were added to the reaction vessel. 4mL of water was added, then 0.3mL of HF was added. This reaction occurred for 4 days at 230°C.

21. $2BaF_2 + MoO_3 + HF$ at 230°C for 4 days with 4mL of water

In this reaction, 0.088g (0.5mmol) BaF_2 and 0.036g (0.25mmol) MoO_3 were added to the reaction vessel. 4mL of water was added, then 0.2mL of HF was added. This reaction occurred for 4 days at 230°C.

22. $BaF_2 + MoO_3 + HF$ at 230°C for 4 days with 4mL of water

In this reaction, 0.088g (0.5mmol) BaF_2 and 0.072g (0.5mmol) MoO_3 were added to the reaction vessel. 4mL of water was added, then 0.2mL of HF was added. This reaction occurred for 4 days at 230°C.

23. $2BaF_2 + 3MoO_3 + HF$ at 230°C for 4 days with 4mL of water

In this reaction, 0.088g (0.5mmol) BaF_2 and 0.108g (0.75mmol) MoO_3 were added to the reaction vessel. 4mL of water was added, then 0.2mL of HF was added. This reaction occurred for 4 days at 230°C.

Results

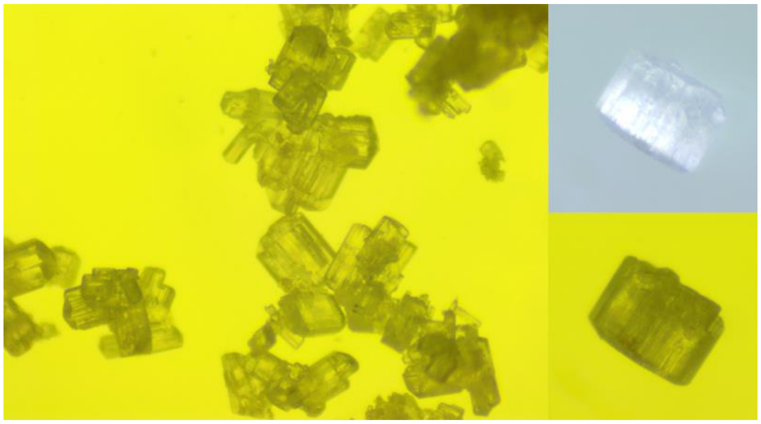

Figure 1: Crystals from reaction 1.

In reaction 1, clear block crystals were obtained, as shown in Figure 1. The top right shows the color of the crystal, while the bottom right shows the shape, and the the left image shows many crystals obtained from this reaction, and shows their transparency.

Figure 2: Crystals from reaction 2.

In reaction 2, pale tan, red-brown, and dark blue sheet crystals were obtained, as seen in Figure 2. These crystals were mixed together throughout the reaction and were not obtained in pure form.

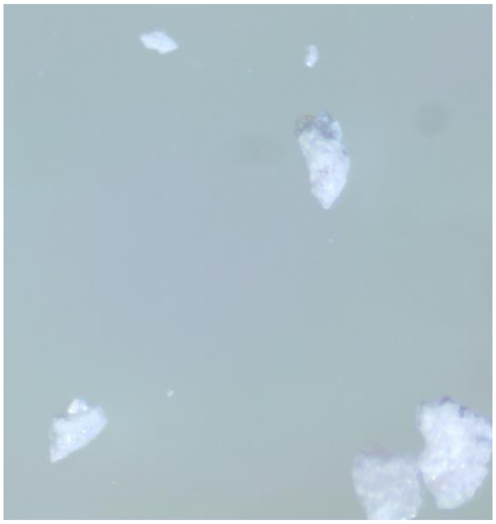

Figure 3: Powder from reaction 3.

In reaction 3, no crystals were obtained. However, a shiny white powder was obtained, as shown in Figure 3.

Figure 4: Powder from reaction 4.

In reaction 4, no crystals were obtained, but a shiny white powder was obtained, as shown in Figure 4.

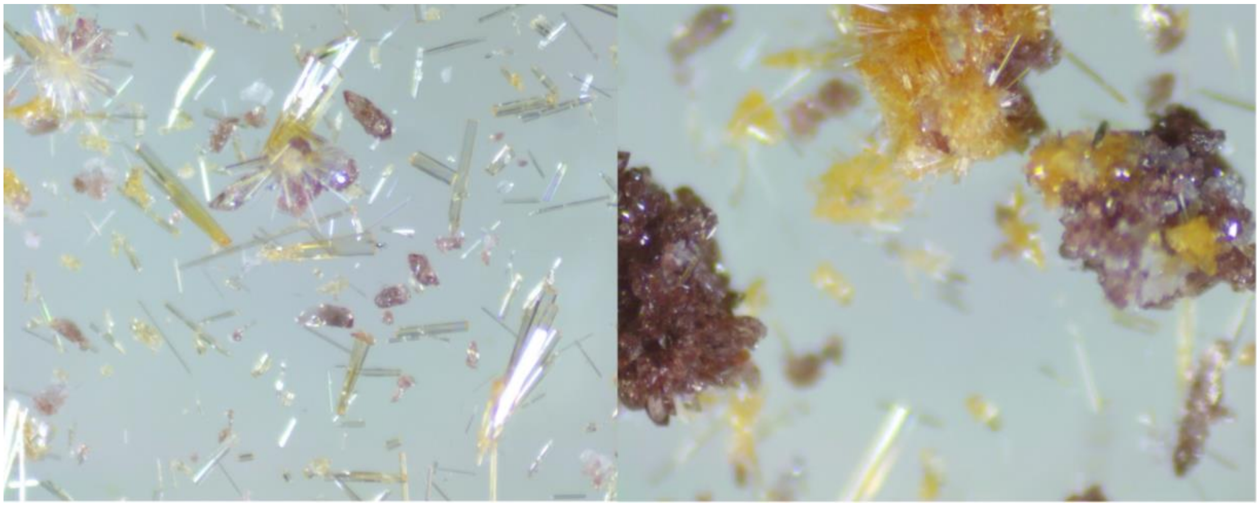

Figure 5: Crystals from reaction 5.

In reaction 5, pale orange and red-brown sheets were obtained, as shown in Figure 5.

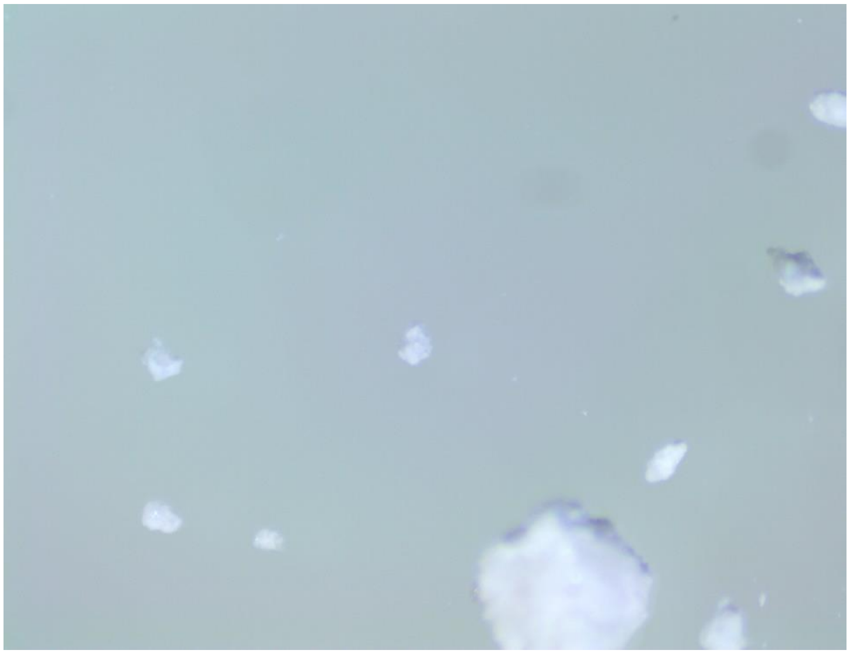

Figure 6: Powder from reaction 6.

In reaction 6, no crystals were obtained, but a white powder was obtained from the reaction, as shown in Figure 6.

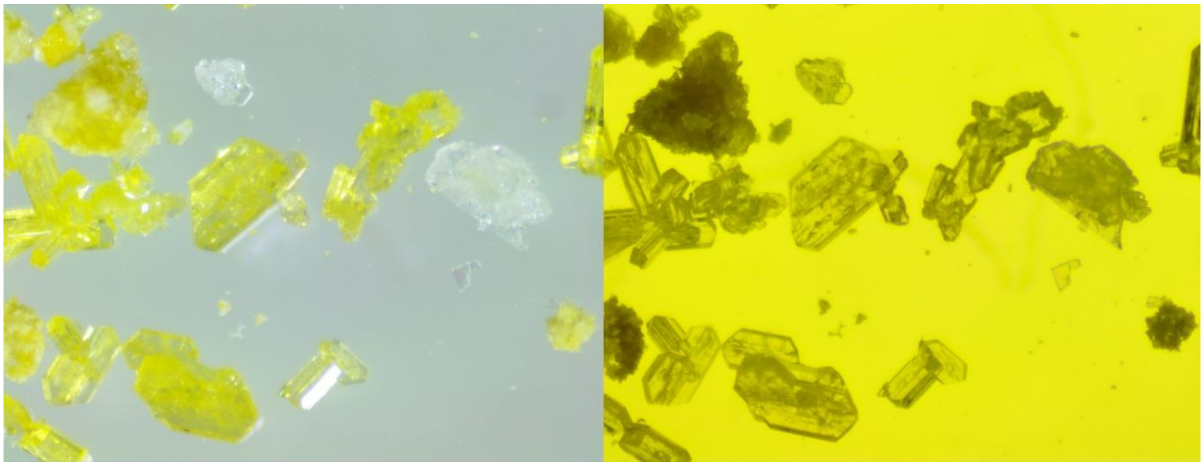

Figure 7: Crystals from reaction 7.

In reaction 7, yellow prism and clear plate crystals were obtained. The color of the crystals can be seen in the left image of Figure 7, while the right image shows the transparency and shape of these crystals. In the right image, many of the yellow and clear crystals appear the same.

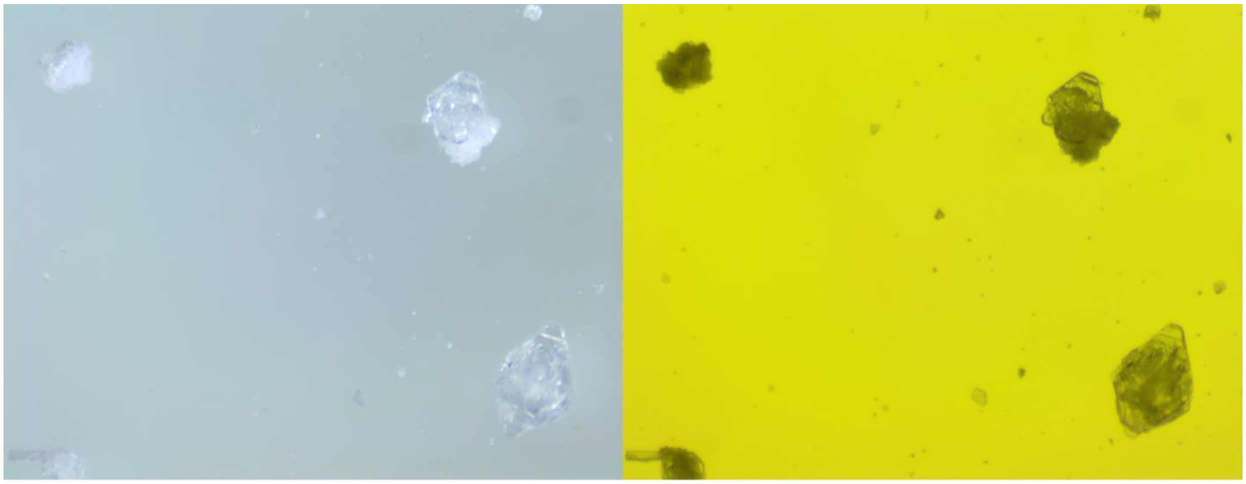

Figure 8: Crystals from reaction 8.

In reaction 8, clear crystals were obtained, as shown in Figure 8. The left image shows the color of the crystals, while the right image shows their transparency.

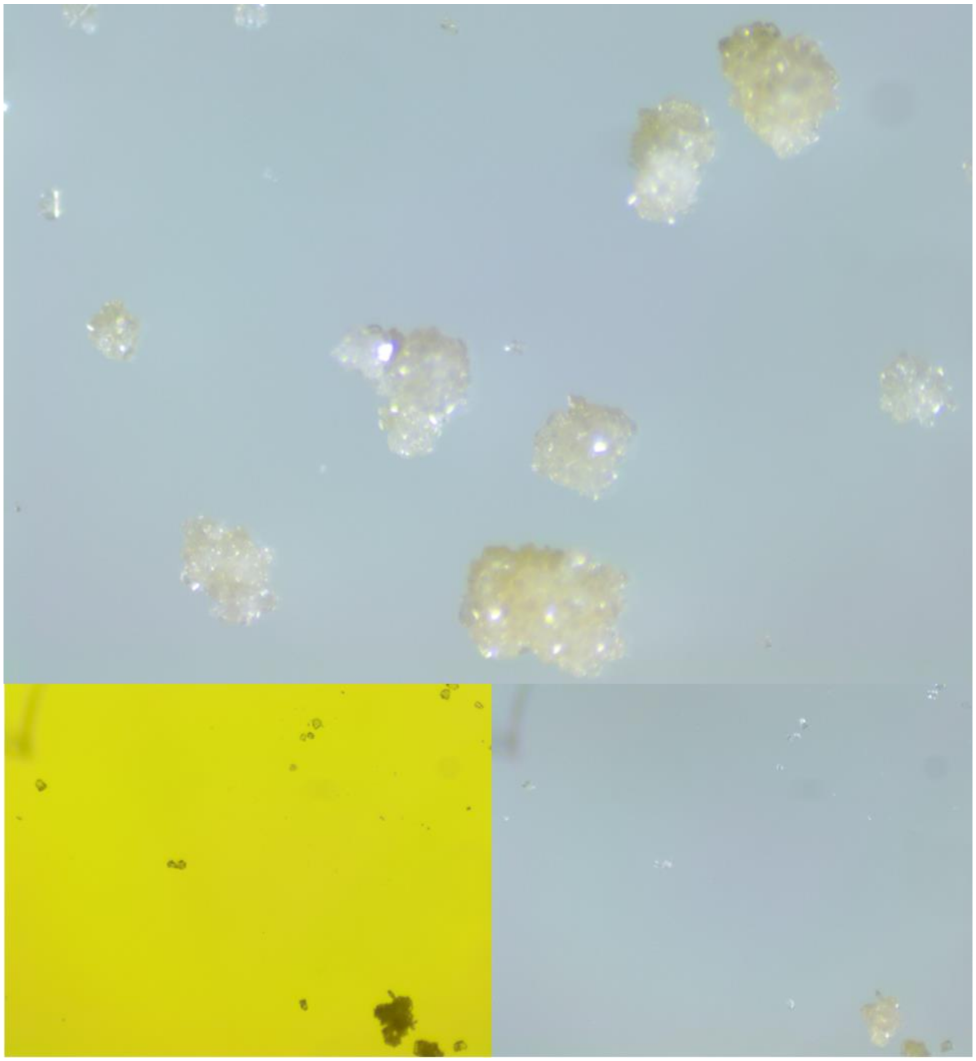

Figure 9: Crystals from reaction 9.

In reaction 9, small clear crystals were obtained. The presence of these crystals can be seen clearly in the bottom left image of Figure 9, toward the top of this image. In the same position, the color of these crystals (clear) can be observed in the bottom right image of Figure 9. The top image shows larger clusters of these crystals, which do not appear colorless, but rather off-white.

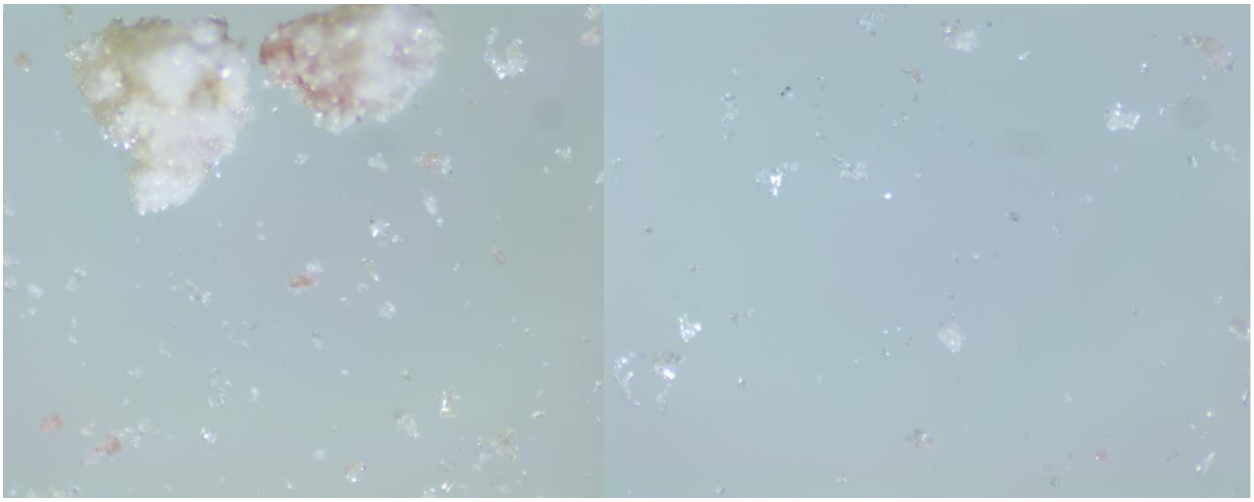

Figure 10: Crystals from reaction 10.

In reaction 10, clear and very lightly colored crystals were observed, as can be seen in Figure 10.

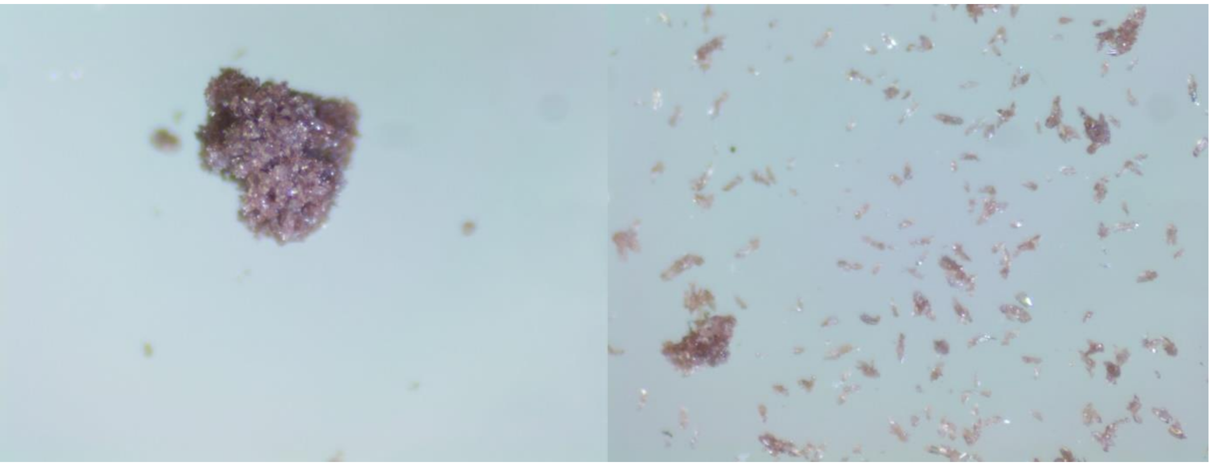

Figure 11: Crystals from reaction 11.

In reaction 11, red-brown crystals were observed, as shown in Figure 11.

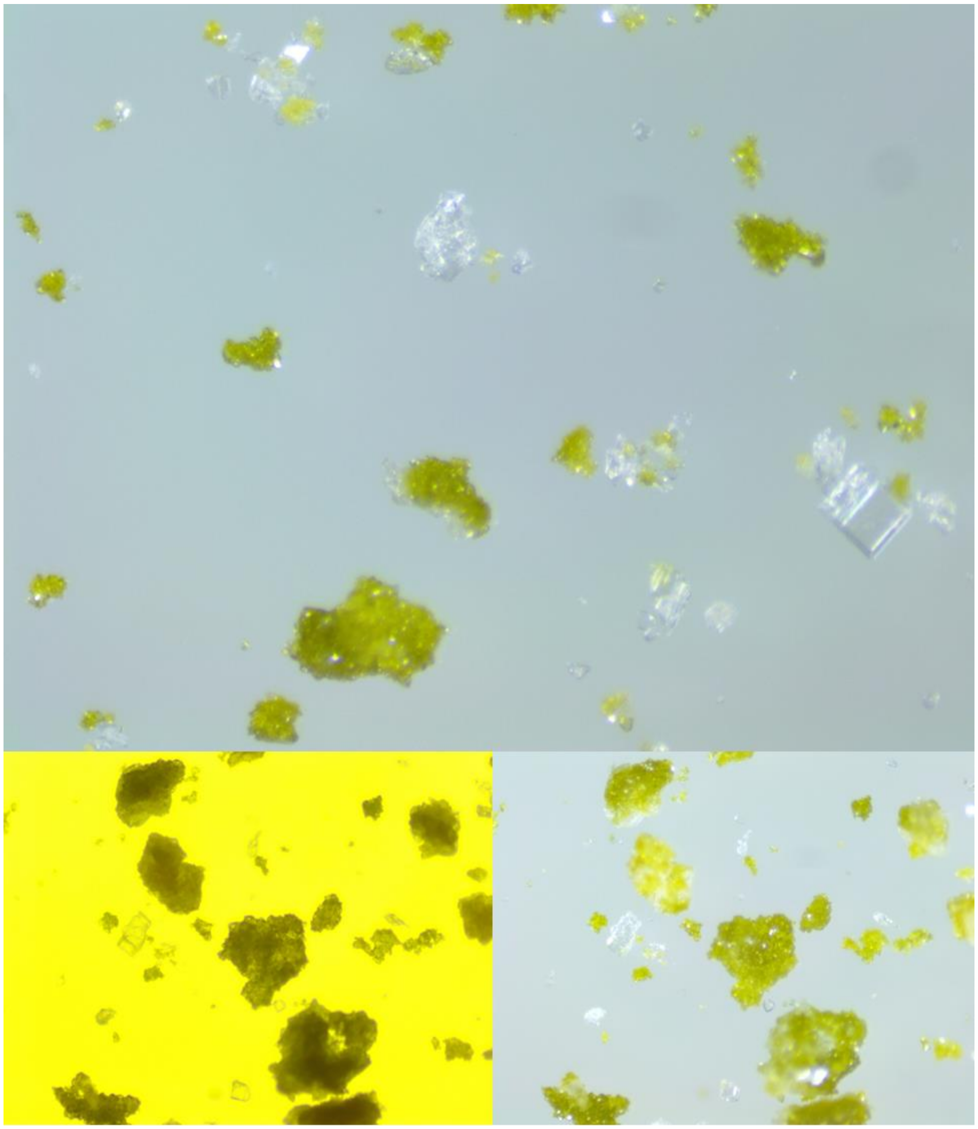

Figure 12: Crystals from reaction 12.

In reaction 12, both yellow-green and clear crystals were observed, as shown in Figure 12. Some of the clear crystals had very distinct shapes, as shown by the cube in the top image of Figure 12. The bottom left image shows the transparency of these crystals, while the bottom right image shows the colors of the same crystals.

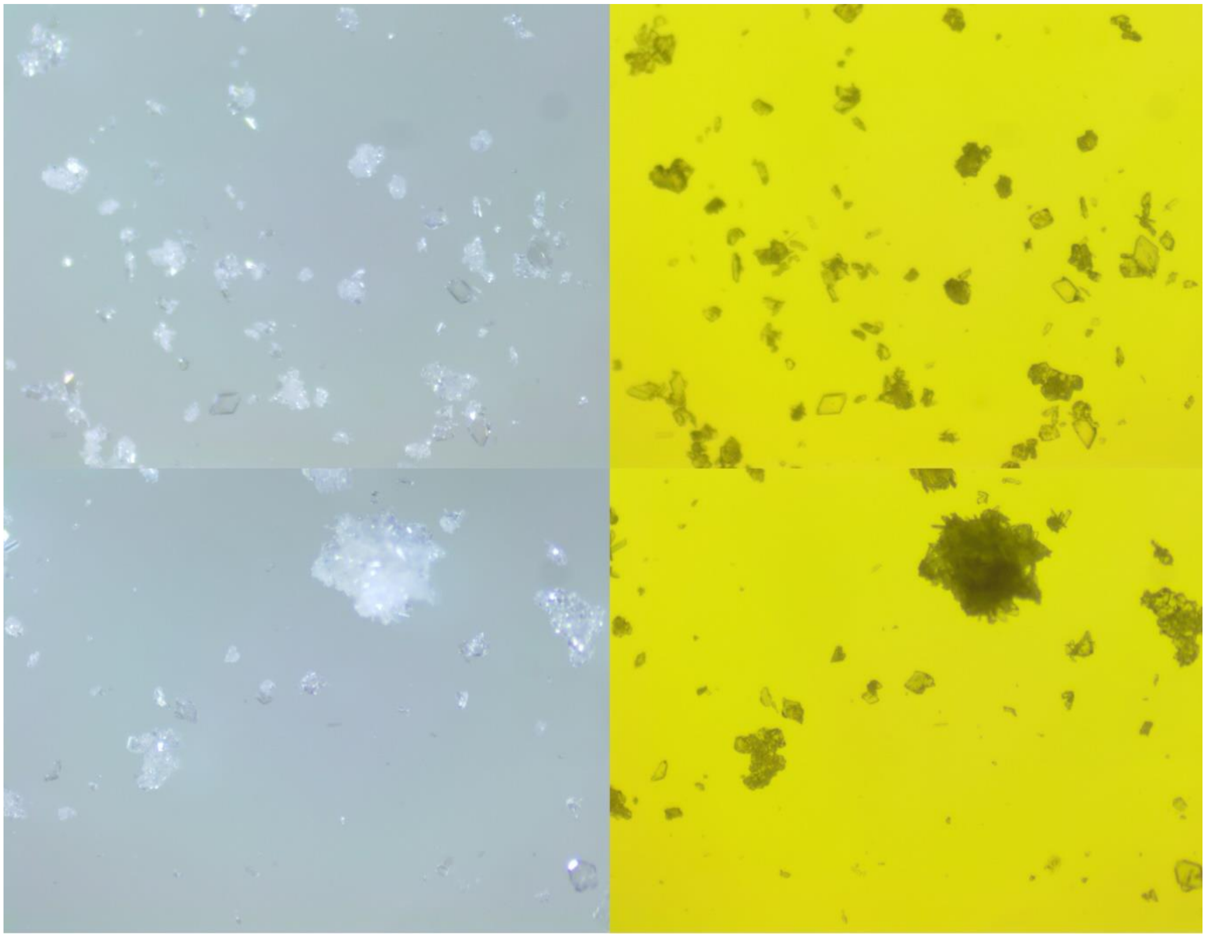

Figure 13: Crystals from reaction 13.

In reaction 13, clear crystals were obtained. The color of the crystals can be seen in the left two images, while a rhombus shape is clearer in the bottom left of the top right image.

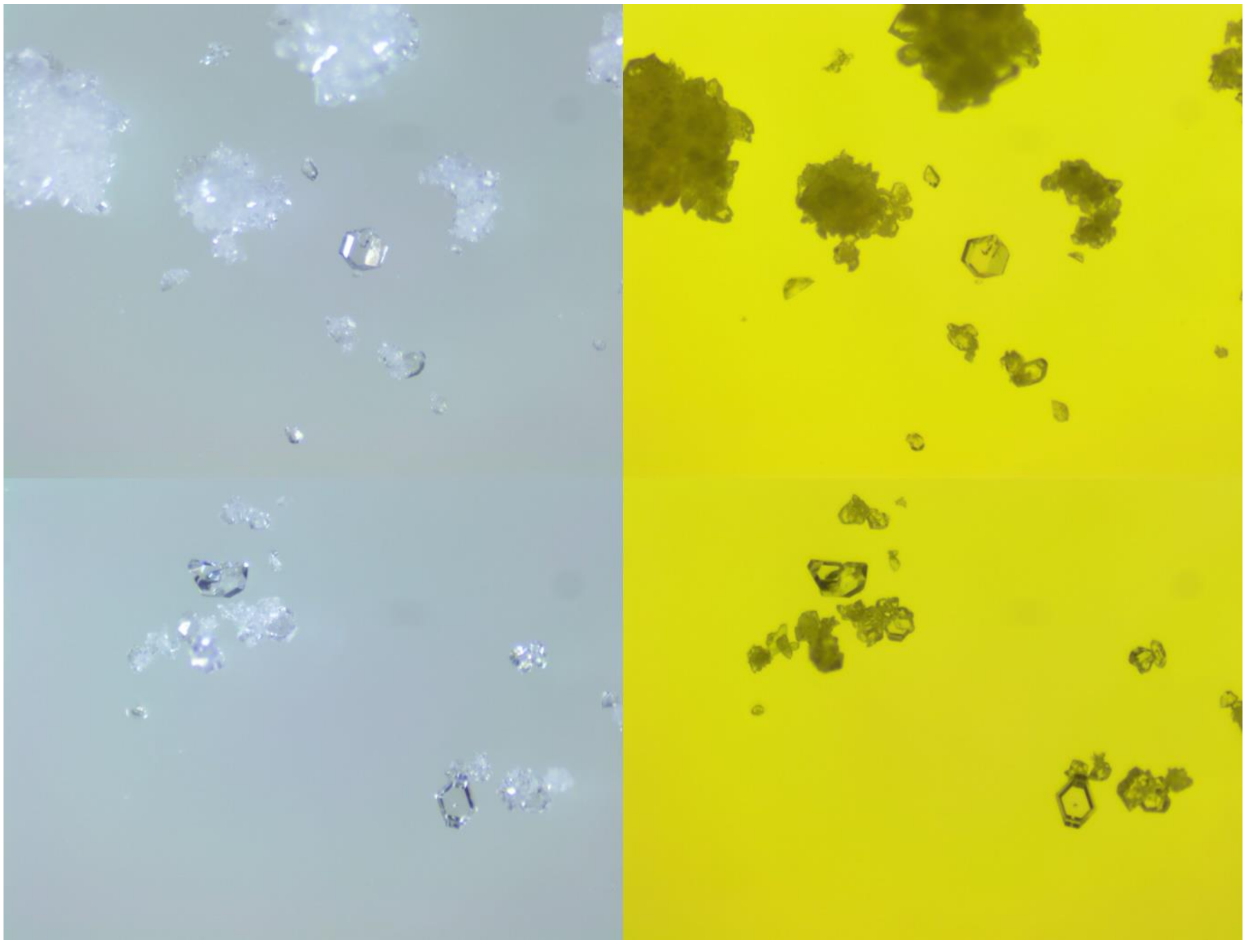

Figure 14: Crystals from reaction 14.

In reaction 14, clear hexagonal crystals were obtained, as shown in Figure 14. The color of the crystals is shown in the left images of Figure 14, while the right images show the shape of the crystals more clearly.

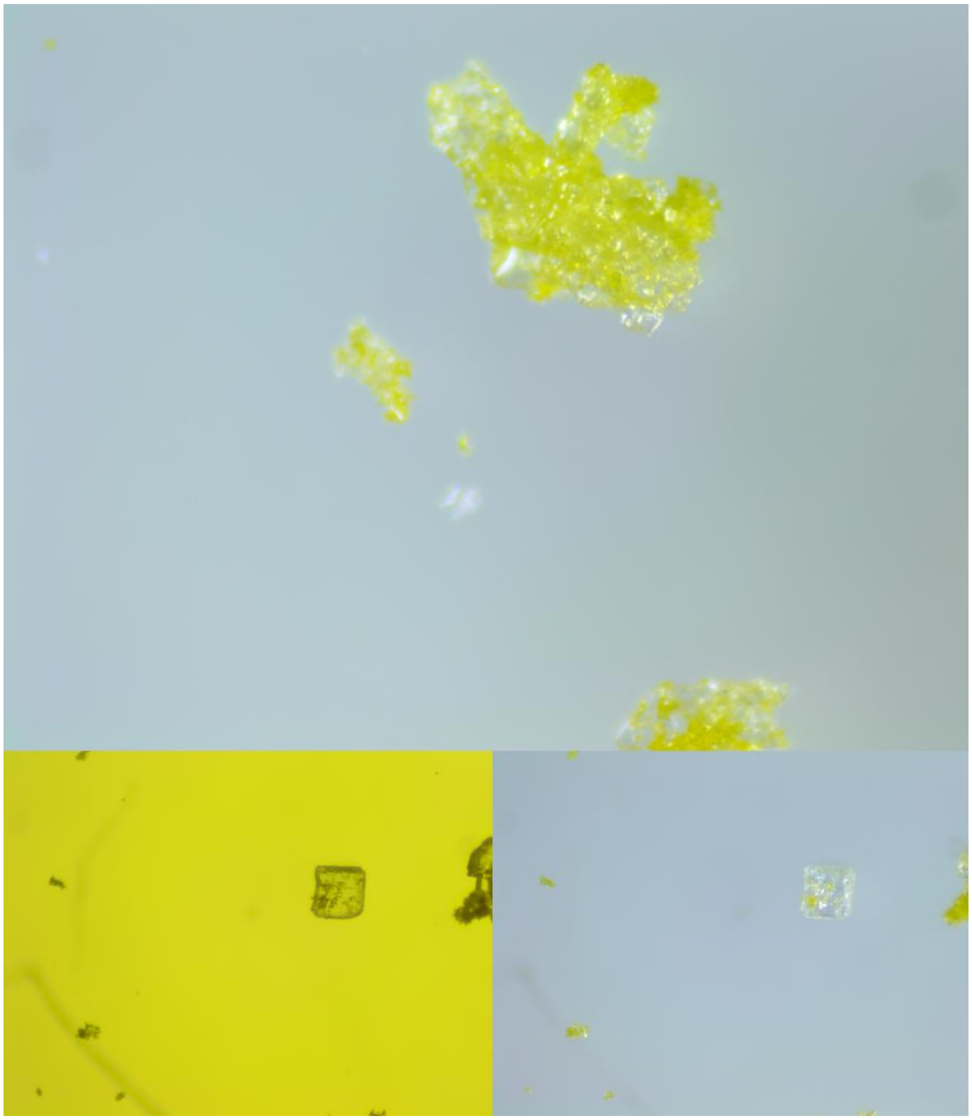

Figure 15: Crystals from reaction 15.

In reaction 15, yellow and clear crystals were obtained. Yellow crystals can be seen in the top image of Figure 15, while the bottom right image shows the color of the clear crystal, which still appears to have some sections that are yellow. The bottom left image shows the transparency and shape of this crystal.

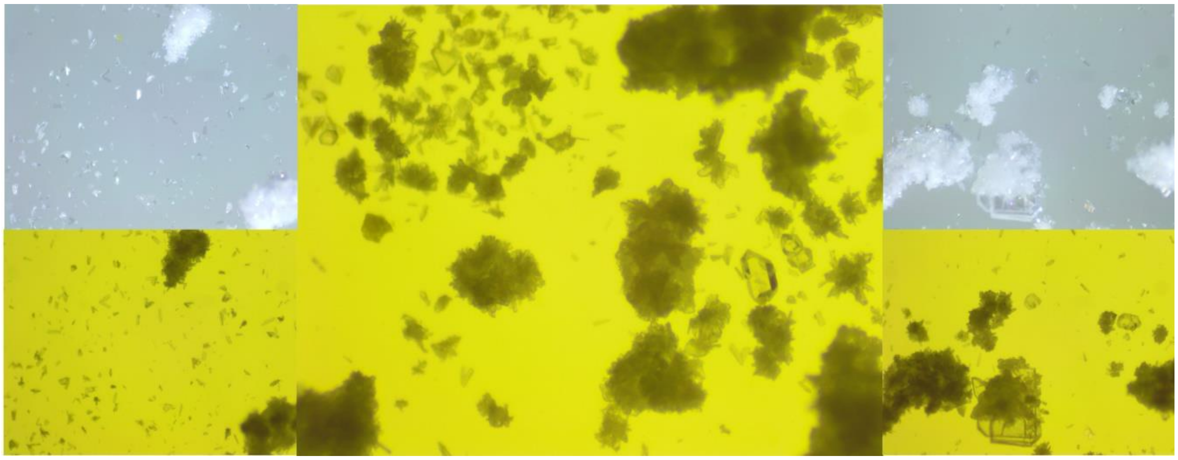

Figure 16: Crystals from reaction 16.

In reaction 16, clear and white crystals were obtained, as shown in Figure 16. The top left and top right images show the color of the crystal, while the bottom left and right images show the shape. The center image shows mainly white crystals, but there are a few clear crystals (which do appear transparent in this image) toward the right of the image.

No crystals were obtained from reaction 17.

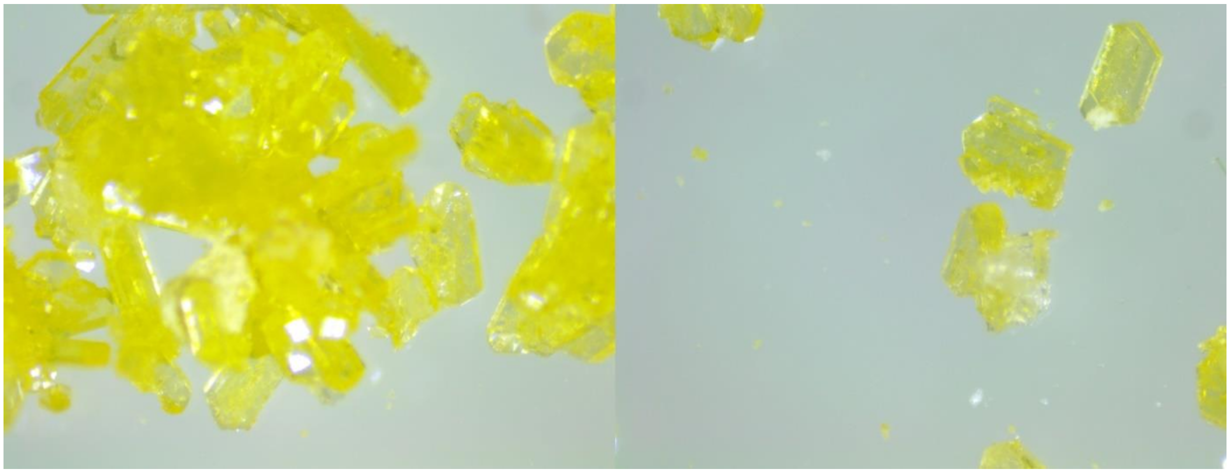

Figure 17: Crystals from reaction 18.

In reaction 18, yellow crystals were obtained, as shown in Figure 17.

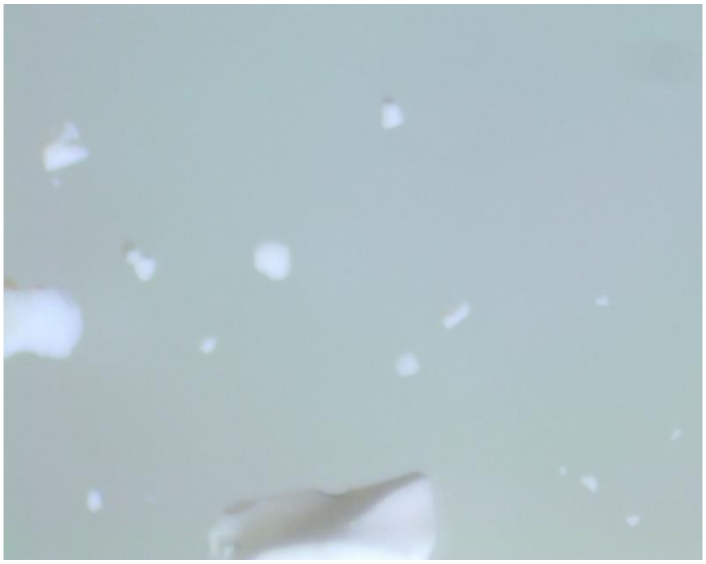

Figure 18: Powder from reaction 19.

In reaction 19, a white powder was obtained, as seen in Figure 18.

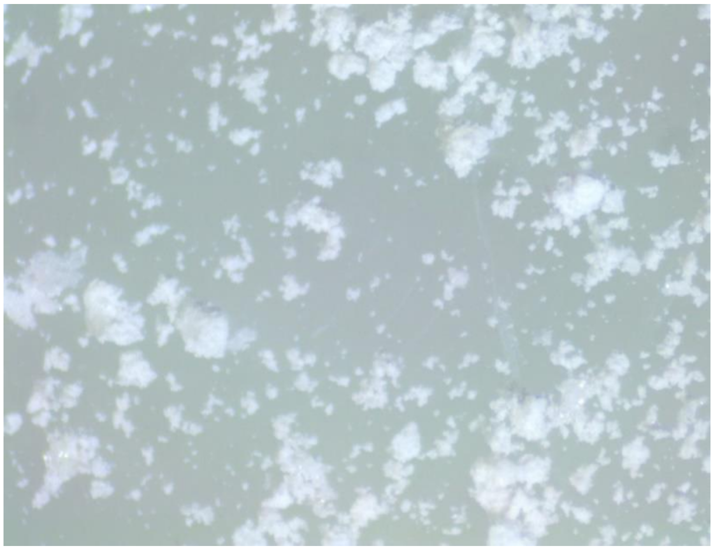

Figure 19: Powder from reaction 20.

In reaction 20, a white powder was obtained, as seen in Figure 19.

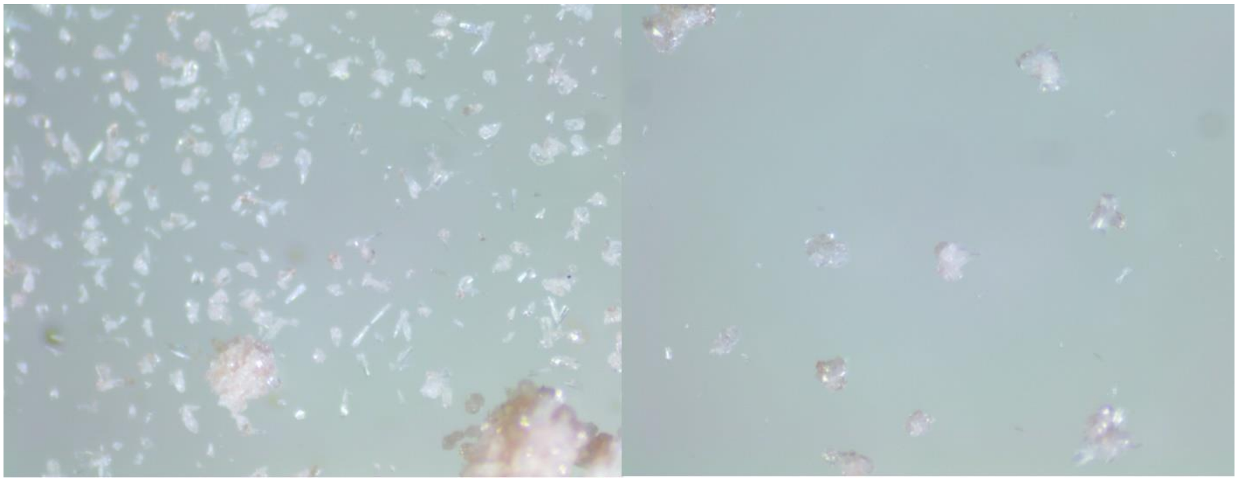

Figure 20: Crystals from reaction 21.

In reaction 21, light pink crystals were obtained, as shown in Figure 20. Smaller crystals, generally, were shown in the left image, while slightly larger clusters of crystals were shown in the right image and a large cluster was shown at the bottom right corner of the left image.

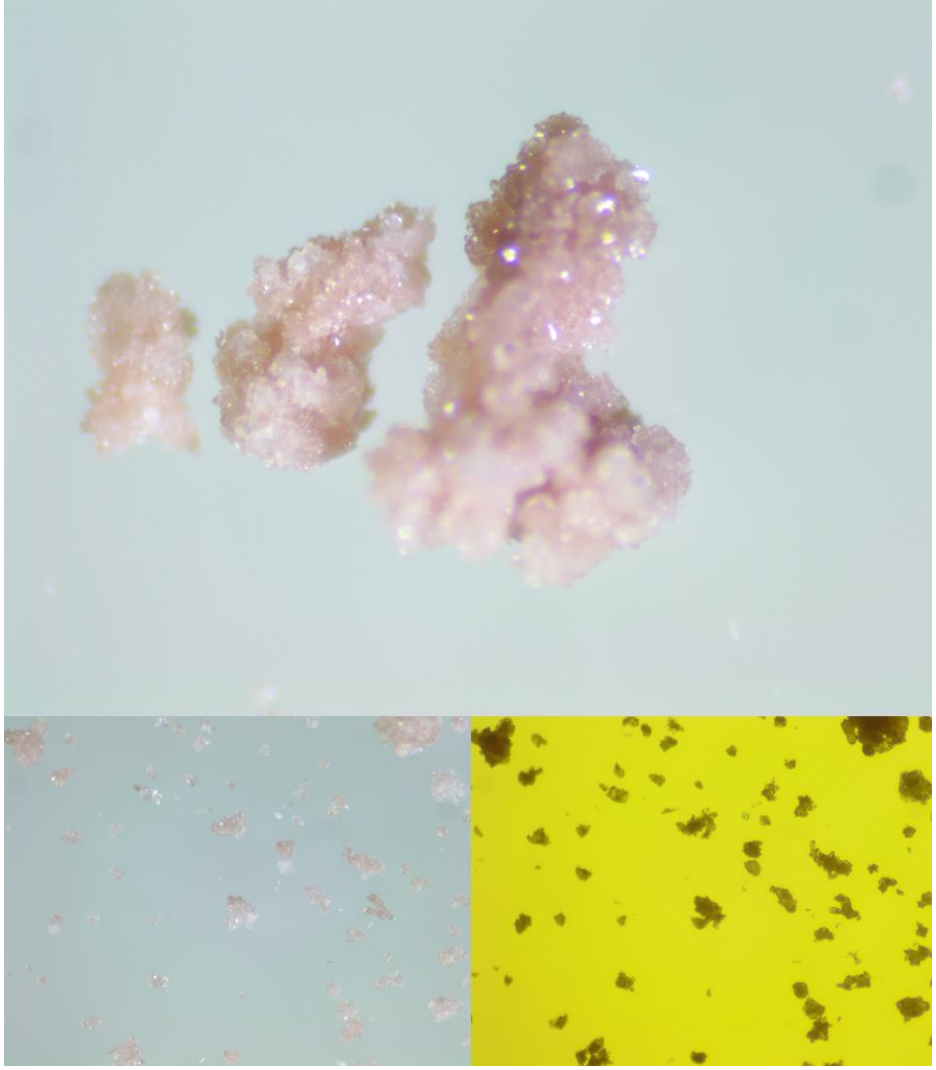

Figure 21: Crystals from reaction 22.

In reaction 22, pink crystals were obtained. These crystals were not particularly transparent, as shown in the bottom right image. There were smaller (in the bottom images) and larger (in the top images) clusters of crystals.

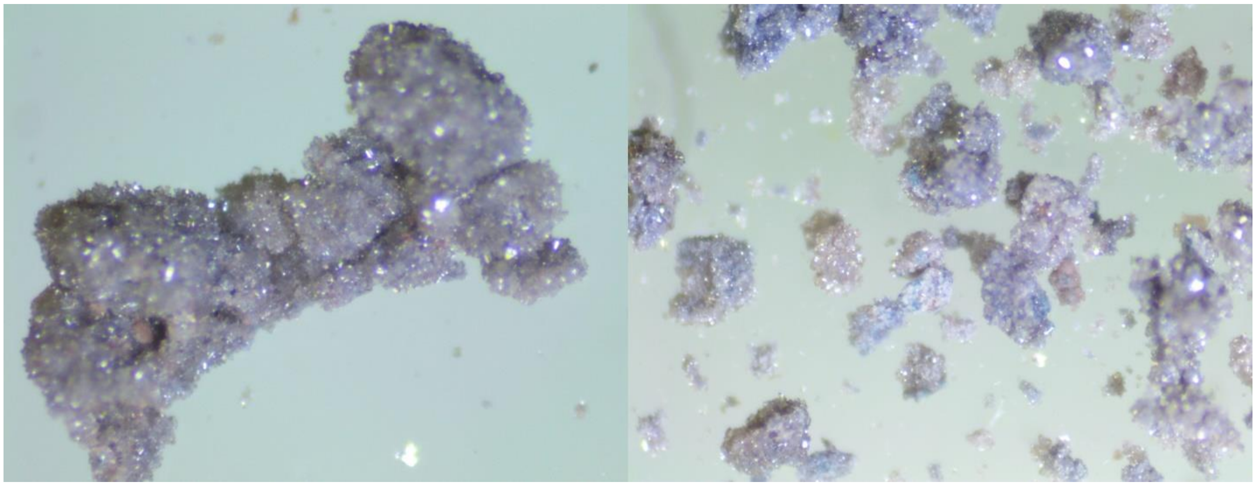

Figure 22: Crystals from reaction 23.

In reaction 23, gray crystals were obtained, as shown in Figure 22. The left image shows a large cluster, while the right image shows smaller crystals.

Discussion

No Solid Product

Overall, only one reaction did not produce any solid product, either powder or crystal. This reaction was reaction 17, in which sodium fluoride was used in place of the barium fluoride that was used in most other reactions. This may be due to the solubility of products that contain sodium, as most compounds with sodium are soluble. Alternatively, it may be due to the difference in size between the sodium and the barium cations.

Powders

Additionally, several products formed powders instead of crystals. These reactions were 3, 4, 6, 19, and 20. Reaction 4 used Na_2CO_3 in place of barium fluoride, reaction 19 used magnesium fluoride in place of barium fluoride, and reaction 20 used cadmium carbonate in place of barium fluoride. The formation of powders, as opposed to crystals in these two reactions may indicate that the barium ion may be important for participation in these reactions. This may be due to the ionic radius of Ba^{2+}, which is larger than those of the other ions that were used in these reactions. These smaller cations may have been too small to coordinate properly with the other reagents.[9] Reactions 3 and 6, which were run under identical conditions with the same molar ratios of the same reagents, however, used barium fluoride, similarly to all the other reactions with successful crystallization, meaning that the failure stemmed from elsewhere. In these reactions, barium fluoride was reacted with tellurite (TeO_2) and hydrofluoric acid. The notable omission from these reactions is any transition metal oxide, particularly d^0 transition metals, which from these results, seems to be important for proper crystallization. This is supported by the literature, where it seems like most, though certainly not all, noncentrosymmetric materials, contain transition metals, and those that don’t often have several other elements that can form several covalent bonds.[5]

Crystals

All reactions not mentioned above produced some form of crystals, though the shapes and colors varied. There were four main groups of reactions done, based on the reagents used. All reactions used hydrofluoric acid and water, in addition to the reagents listed. The first group included reactions 1, 2, 5, 9, 10, and 11, which used the reagents barium fluoride, molybdenum (VI) oxide, and tellurite. The second group included reactions 7, 12, 15, and 18, which used the reagents barium fluoride, vanadium (V) oxide, and iodine pentoxide. The third group included reactions 8, 13, 14, and 16, which used the reagents barium fluoride, molybdenum (VI) oxide, and iodine pentoxide. The fourth group included reactions 21, 22, and 23, which used the reagents barium fluoride and molybdenum (VI) oxide.

Reactions with barium fluoride, molybdenum (VI) oxide, and tellurite

In reactions 1, 2, and 5, there was less liquid in the reaction vessel, and the hydrofluoric acid was a higher concentration of the liquid in the reaction vessel, as there was 0.25mL of HF and only 1mL of water. Reaction 1 was a 1:1:1 molar ratio of BaF_2 to MoO_3 to TeO_2. This reaction resulted in clear block crystals, as seen in Figure 1. Reaction 2 was a 1:2:1 molar ratio of BaF_2 to MoO_3 to TeO_2, and this resulted in brown and tan sheets, as seen in Figure 2. Reaction 5 was a replication of reaction 1, but it resulted in results more similar to those from reaction 2. This may have been due to the use of a different oven between reaction 1 and reaction 5, which may have changed the results, or to very slight differences in masses as measured on the analytical balance all adding up to make a notable difference in the crystals produced.

In reactions 9, 10, and 11, more liquid was present and the hydrofluoric acid was a lower concentration, as there was 0.1mL, 0.25mL, and 0.5mL of HF, respectively, and 4mL of water, in each of these reaction vessels. Each of these reactions had a 1:1:1 molar ratio of BaF_2 to MoO_3 to TeO_2. Reaction 9 resulted in clear and off-white crystals, reaction 10 resulted in clear and light pink crystals, and reaction 11 resulted in red-brown crystals.

Overall, in these reactions, it seems as though the concentration of hydrofluoric acid made notable differences in the crystals that were obtained. Between reactions 9, 10, and 11, the hydrofluoric acid concentration increased, and as it did, the color of the large crystals became darker. Additional differences were noted between reactions 1, 2, and 5 and reactions 9, 10, and 11, which had different ranges of HF concentration. Reactions 2 and 5 had brown and tan sheets, and reaction 1 had block crystals, all of which had more discernable shapes (particularly for reactions 1 and 5) than the crystals formed in reactions 9, 10, and 11. Additional color differences were noted, most obviously between reaction 1 and all other reactions. The color of the crystals formed in reaction 11, can be compared to the large clusters of darker red-brown crystals formed in both reaction 2 and particularly reaction 5. This comparison can be seen in Figure 23. Temperature and time of reaction were kept the same for all of these reactions, so their effects were not compared.

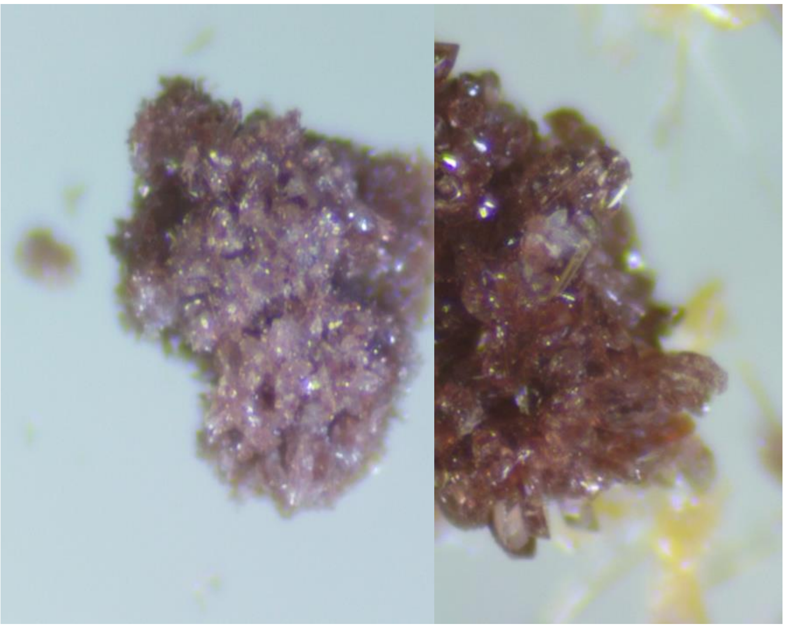

Figure 23: Side-by-side comparison of red-brown crystals from reaction 11 in the left image and 5 in the right image, provided for convenience.

Reactions with barium fluoride, vanadium (V) oxide, and iodine pentoxide

Reactions 7, 12, 15, and 18 each occurred with a 4:1:2 ratio of BaF_2 to V_2O_5 to I_2O_5 with 4mL of water. Reaction 7 occurred for 3 days at 200°C with 0.3mL of HF. This produced mainly yellow crystals with some clear crystals. Reaction 12, 15, and 18 occurred for 4 days at 230°C. 0.3mL of HF was added to reaction 12, which also produced yellow and clear crystals. 0.15mL of HF was added to reaction 15, which produced yellow and clear crystals. Reaction 18 was done the same as reaction 12, but it produced only yellow crystals, with no (or very few) clear crystals.

All of these reactions resulted in very similar yellow and clear crystals, regardless of the specific concentration of hydrofluoric acid and specific reaction conditions used, within the constraints of what was attempted in these experiments.

Reactions with barium fluoride, molybdenum (VI) oxide, and iodine pentoxide

All of these reactions occurred for 4 days with 4 mL of water. Reaction 8 occurred with a 2:2:1 ratio of BaF_2 to MoO_3 to I_2O_5 and 0.3mL of HF at 200°C. This resulted in clear rhombus crystals and some white crystals. Reaction 13 occurred with a 2:2:1 ratio of BaF_2 to MoO_3 to I_2O_5 and 0.2mL of HF at 230°C, and this resulted in small clear rhombus crystals and larger clumps of white crystals. Reaction 14 occurred with a 2:2:1 ratio of BaF_2 to MoO_3 to I_2O_5 and 0.4mL of HF at 230°C. This reaction resulted in white clumps and clear hexagonal crystals. Reaction 16 occurred with a 4:4:1 ratio of BaF_2 to MoO_3 to I_2O_5 and 0.15mL of HF at 230°C, resulting in clear and white crystals.

Reactions 13, 14, and 16 resulted in small clear crystals and larger clumps of crystals being white. This seems to be due to the higher temperature, as it was not observed in reaction 8, which occurred at a lower temperature. Additionally, the higher concentration of hydrofluoric acid in reaction 14 produced hexagonal crystals, while the lower concentrations seemed to produce rhombus crystals, and the lowest concentration did not produce repetitively discernable shapes of crystals.

Reactions with barium fluoride and molybdenum (VI) oxide

These reactions all occurred at 230°C for 4 days with 0.2mL of hydrofluoric acid and 4mL of water. Reaction 21 occurred with a 2:1 ratio of BaF_2 to MoO_3, which resulted in clear and light pink crystals. Reaction 22 occurred with a 2:2 ratio of BaF_2 to MoO_3, which resulted in pink crystals. Reaction 23 occurred with a 2:3 ratio of BaF_2 to MoO_3, which resulted in purple-gray crystals.

These reactions seem to indicate that as the ratio of barium fluoride to molybdenum (VI) oxide decreased, the color of the crystals got darker, which may indicate a change in the composition of the crystals. As all other factors were held constant, their effects were not known.

Conclusion

More analysis using single crystal x-ray diffraction would need to be done to determine the composition and structure of the crystals that were synthesized. Determination of the crystal composition would also allow for direct comparison of the reaction, as the chemical makeup of the compounds could be compared to one another. This is in addition to comparing the appearance of the crystals that were formed by reactions, which may be similar, even if the products are not the same. This step is particularly important, as it would allow for the determination of whether the products that were synthesized were new. For any materials that were novel, more analysis would need to be done, as detailed below.

Other methods, such as powder x-ray diffraction, could be used to check the purity of crystals, particularly once their structure is known by comparing the experimental data to the calculated patterns for that specific material. Thermogravimetric analysis could also be used to determine the processes of decomposition and compare these to other noncentrosymmetric materials. UV-Vis and IR spectroscopy could be used to determine the wavelength ranges at which crystals absorbed light, as opposed to their ranges of transparency. Additionally, second-harmonic generation measurements could be taken to compare these crystals to other noncentrosymmetric crystals.

In addition to the increased analysis of the previously synthesized crystals, in the future, more variations could always be made to the temperatures, molar ratios and reagent combinations in an attempt to synthesize novel noncentrosymmetric materials.

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