MRL

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# Inorganic-Organic hybrid materials consisting of a network using carboxylic acids as the connections between metal ions/metal ion clusters.

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**Funding: Unilever & NSF**

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National Science Foundation
WHERE DISCOVERIES BEGIN

# Introduction:

The purpose of this project is to utilize single or heterogeneous phase reactions in aqueous media at elevated temperatures and pressure in order to crystallize inorganic and organic hybrids.

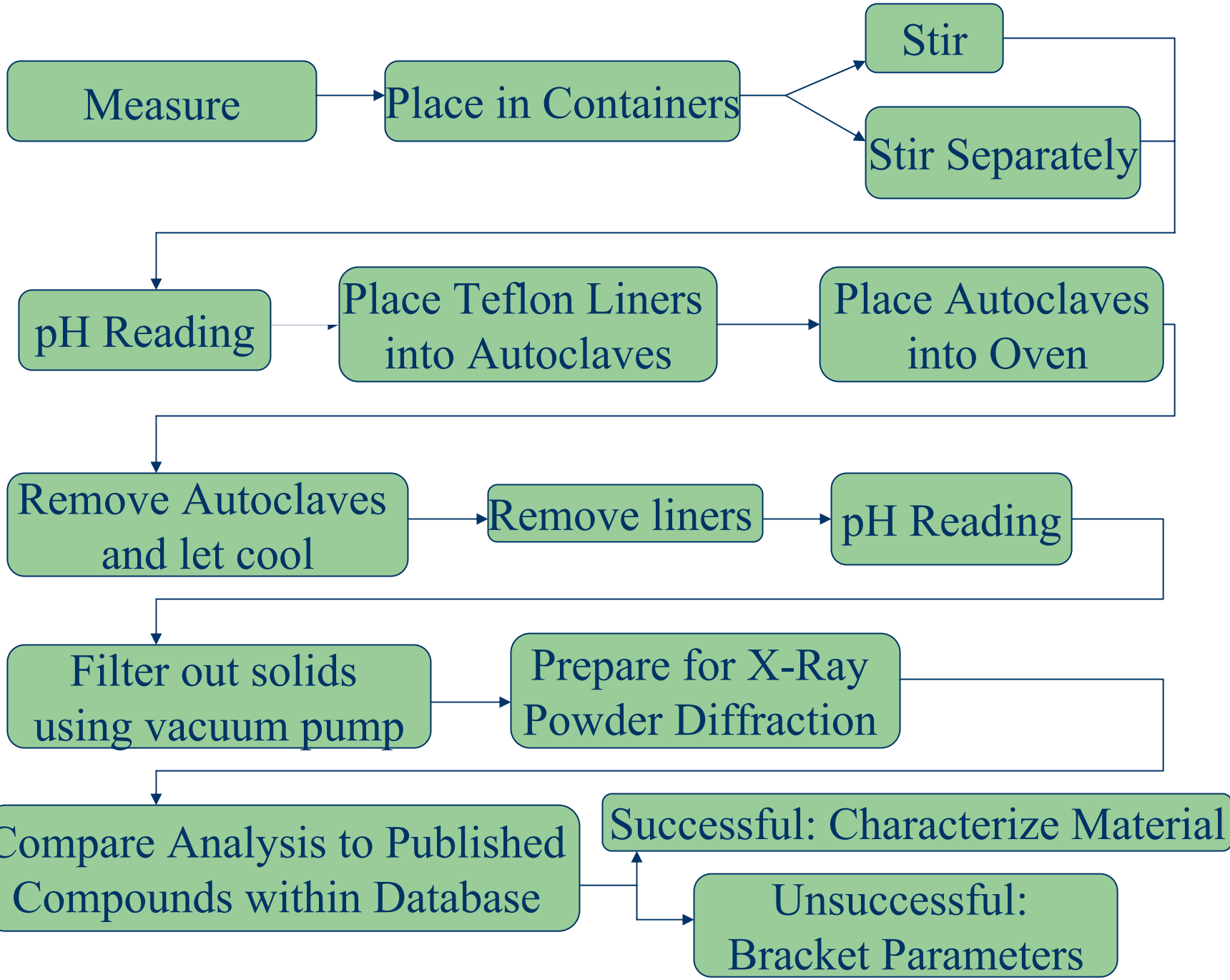
What is a crystal?

Crystals are solids containing atoms arranged in a pattern that repeats periodically in 3-dimensions.

Table Salt: $Na^+ + Cl^- = NaCl$

# Research Methods:

| |
|---|
| ●**Hydrothermal Synthesis** is carried out by the use of aqueous media that is heated to temperatures above 100º C and at self-induced pressure. |
| ●**Solution Chemistry** is similar to hydrothermal processes, but is heated to temperatures below 100º C and not necessarily in sealed containers. |
| ●**Solvothermal Biphasic Synthesis** utilizes the interphase between two different solutions being separated by their densities. Reactions/crystal growth occurs with the same type of heating and pressure conditions as a hydrothermal process. |


Measure
Place in Containers
Stir
Stir Separately
pH Reading
Place Teflon Liners into Autoclaves
Place Autoclaves into Oven
Remove Autoclaves and let cool
Remove liners
pH Reading
Filter out solids using vacuum pump
Prepare for X-Ray Powder Diffraction
Compare Analysis to Published Compounds within Database
Successful: Characterize Material
Unsuccessful: Bracket Parameters

# Results:

1. Iron (III) Benzenetricarboxylate, to form iron analogs of indium structures.

- Produced a compound that was not an analog nor very crystalline.

2. Manganese Succinates, to reproduce earlier work in order to determine its crystal structure.

- Produced a combination of Hausmannite ($Mn_3O_4$) and Pyrolusite ($MnO_2$).

3. Manganese Carboxylate Molecular Magnetic Clusters, to create a framework that links clusters from a previous work.

- Produced a re-crystallization of Succinic Acid ($HO_2CCH_2CH_2CO_2H$) and Adipic Acid ($HO_2C(CH_2)_4CO_2H$).

# Instruments:

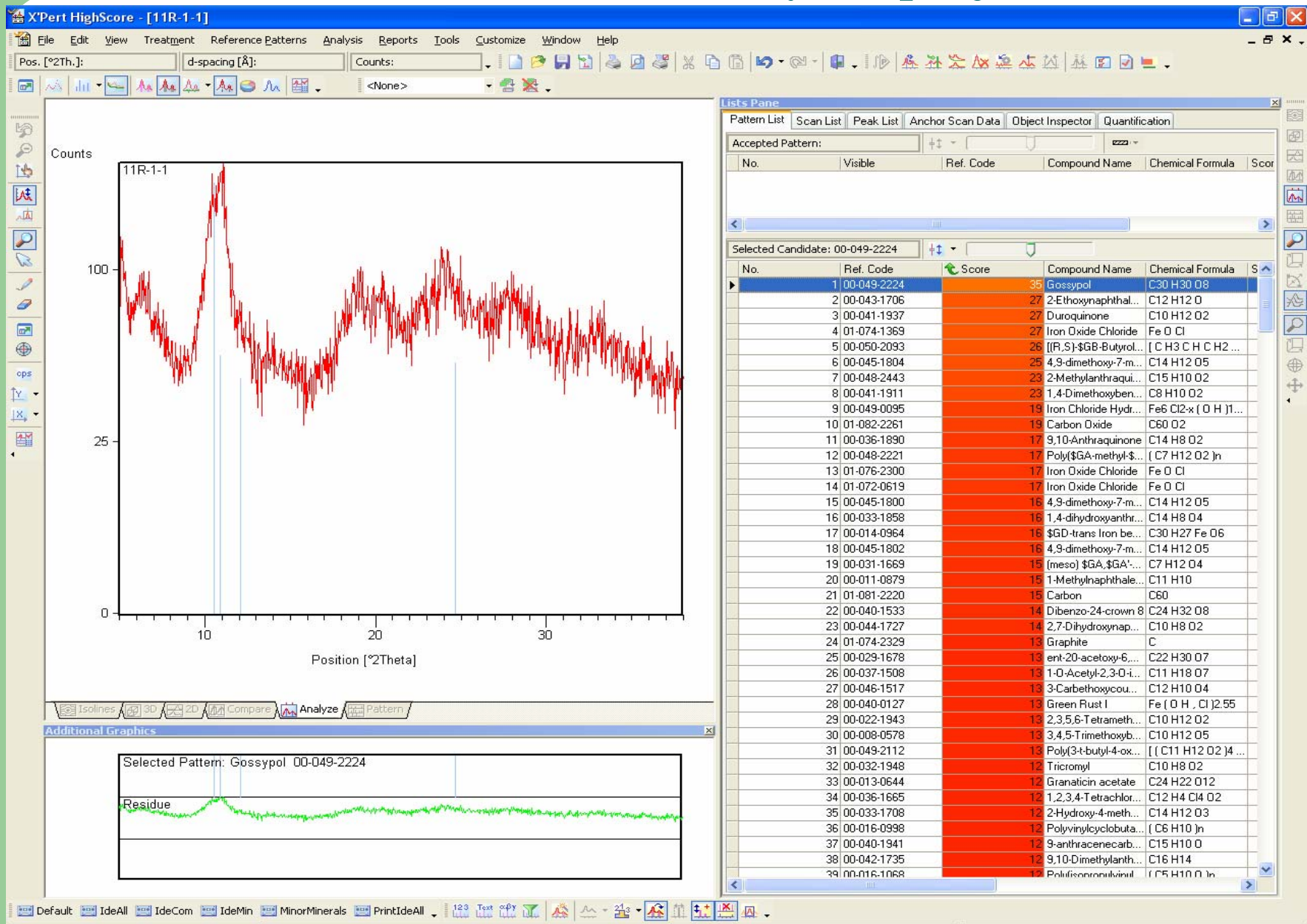
- Philips X'PERT MPD (Diffractometer)

**Computer Programs:**

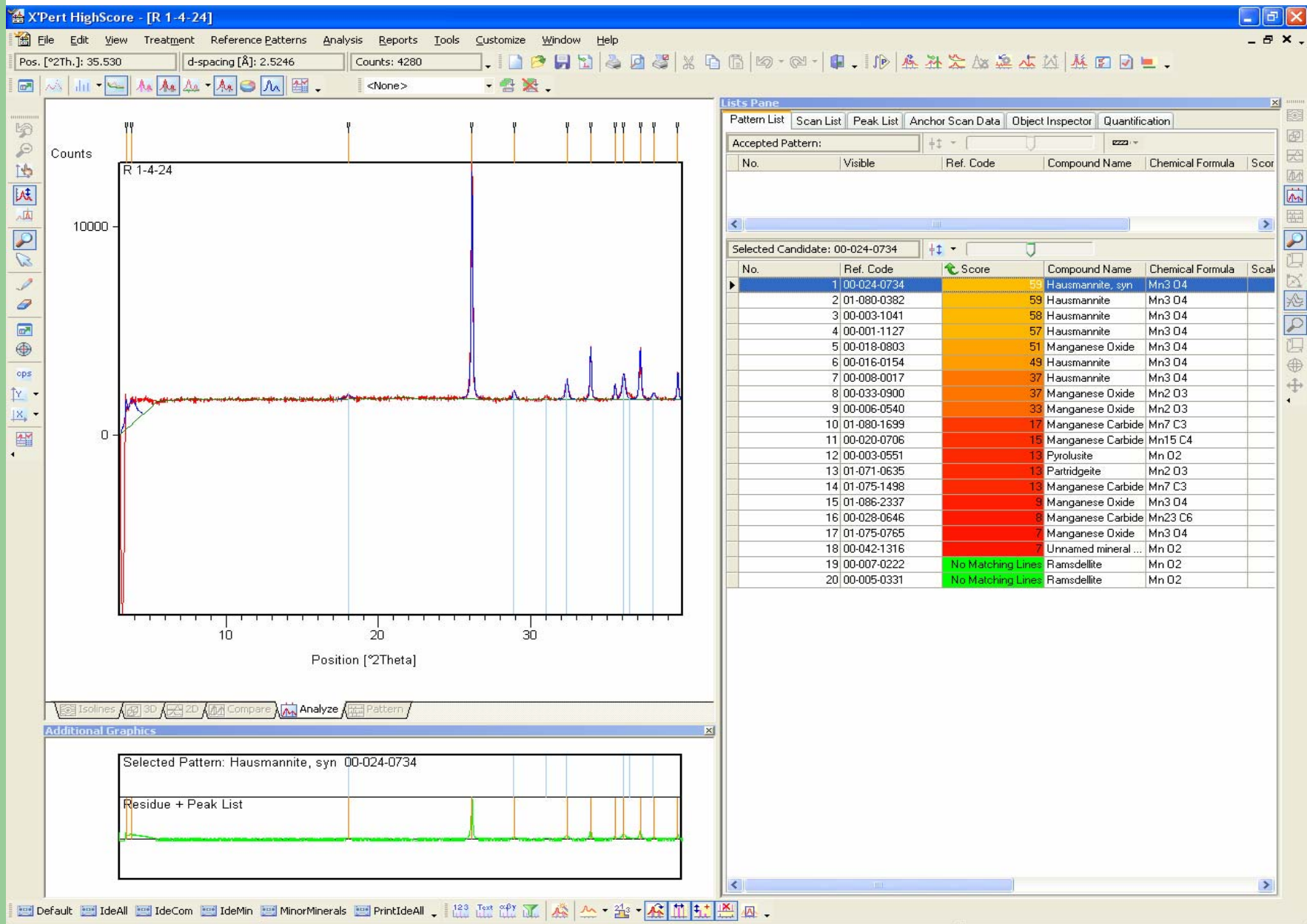
- X'Pert High Score
- X'Pert Data Collector
- Conquest
- Diamond.

# Analysis:

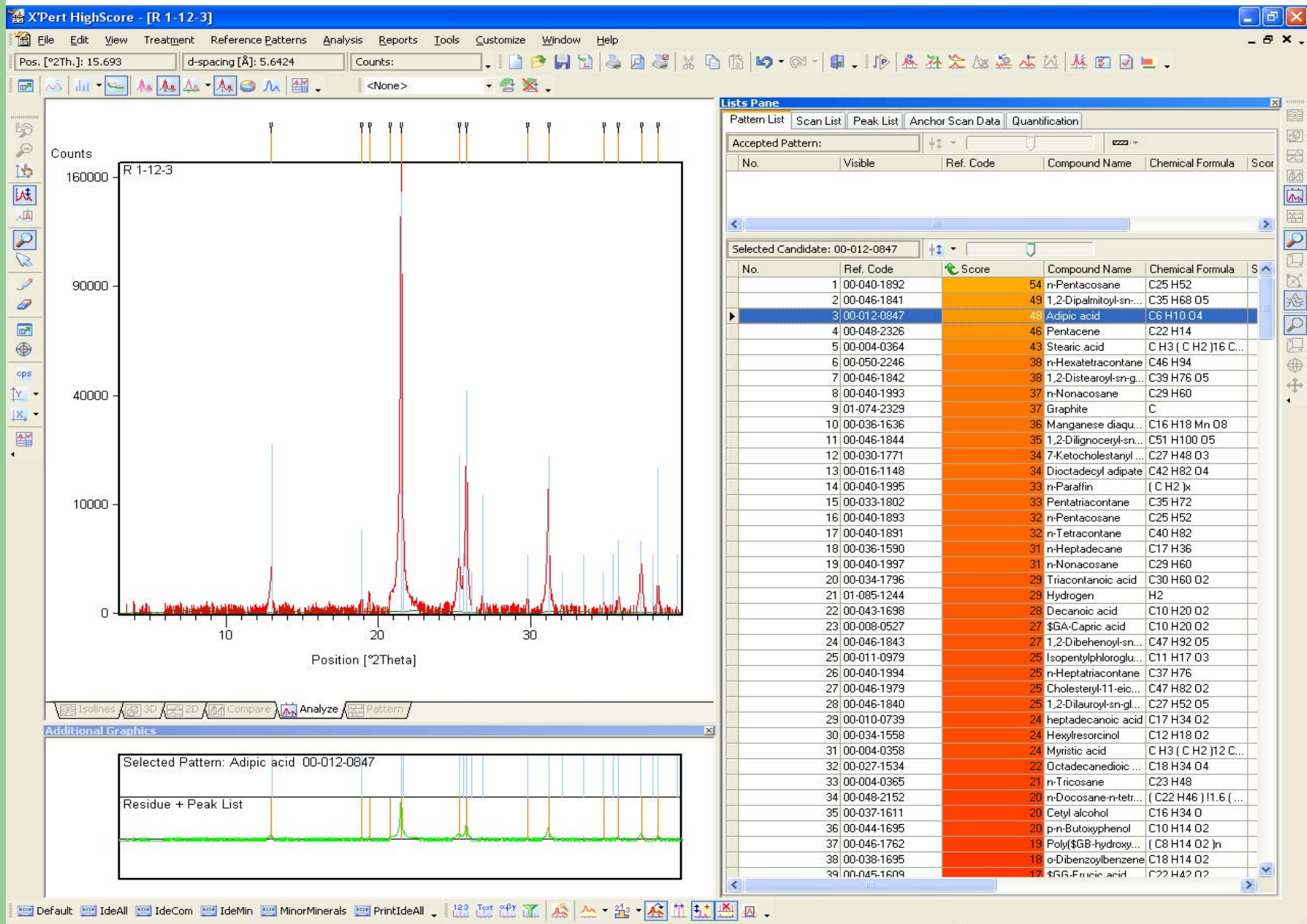
## Powder diffraction pattern for Iron (III) Benzenetricarboxylate project (R 1-1-11).



# Powder diffraction pattern for Manganese Succinate project (R 1-4-24).



# Powder diffraction pattern for Manganese Carboxylate Molecular Magnetic Clusters project (R 1-12-3).



# Conclusion:

By conducting numerous experiments with the goal of producing an inorganic-organic hybrid crystal, I was unsuccessful at all attempts. I have concluded that my research findings are inclusive and require more time to bracket parameters in order to obtain the desired results.

- Iron (III) Benzenetricarboxylate, to form iron analogs of indium structures, may not have been produced because the cooling rate may have been to rapid.
- Manganese Succinates, to reproduce earlier work in order to determine its crystal structure, may not have been produced because vital information was unavailable.
- Manganese Carboxylate Molecular Magnetic Clusters, may not have been produced because the soak time may have been extended over its threshold.

# Iron (III) Benzenetricarboxylic Acid, to form iron analogs of indium structures (R 1-1)

| Sample # | Pyridine | Salt | Acid | Water | pH In/out | Time In/out |
|---|---|---|---|---|---|---|
| 10 | 0.34 g | 0.277 g | 0.17 ml | 5.02 ml | 4.37/? | 10:42 am/ 2:50 pm |
| 11 | 0.31 g | 0.277 g | 2.147 ml | 5.03 ml | 4.17/ 4.13 | Same |
| 15 | 0.31 g | 0.274 g | 0.246 ml | 5.04 ml | 4.04/ 2.69 | Same |

| | Chemical Formula: | FW: |
|---|---|---|
| Salt: Iron (III) Chloride Hexahydrate | $FeCl_3\ 6H_2O$ | 270.3 g/M |
| Acid:Benzenetricarboxylic Acid | $C_6H_3(Co2H)_3$ | 210.14 g/M |
| Pyridine | $C_5NH_5$ | 79.05 g/M |
| Water: Deionized Water | $H_2O$ | 18.00 g/M |

T = 125° C for 100.13 hrs

# Manganese Succinates, to reproduce earlier work in order to determine its crystal structure.

| Sample # | Salt | Base | Acid | pH In/out | Water | Time |
|---|---|---|---|---|---|---|
| NC3 | 0.196 g | 7/1 drops | 0.234g | 8.59/ 5.56 | 5.03 ml | 2:27 |
| 23 | 0.198 g | 8/23 drops | 0.237g | 9.94/ 7.77 | 5.0 ml | same |
| 26 | 0.197 g | 11/4 drops | 0.237g | 12.96/ 12.88 | 5.02 ml | same |

| | Chemical Formula: | FW: |
|---|---|---|
| Salt: Manganese (II) Chloride | $MnCl_2 4H_2O$ | 196.00 g/M |
| Base: Potassium Hydroxide | KOH | 56.11 g/M |
| Acid: Succinic Acid | $HO_2CCH_2CH_2CO_2H$ | 118.09 g/M |
| Water: Deionized Water | $H_2O$ | 18.00 g/M |

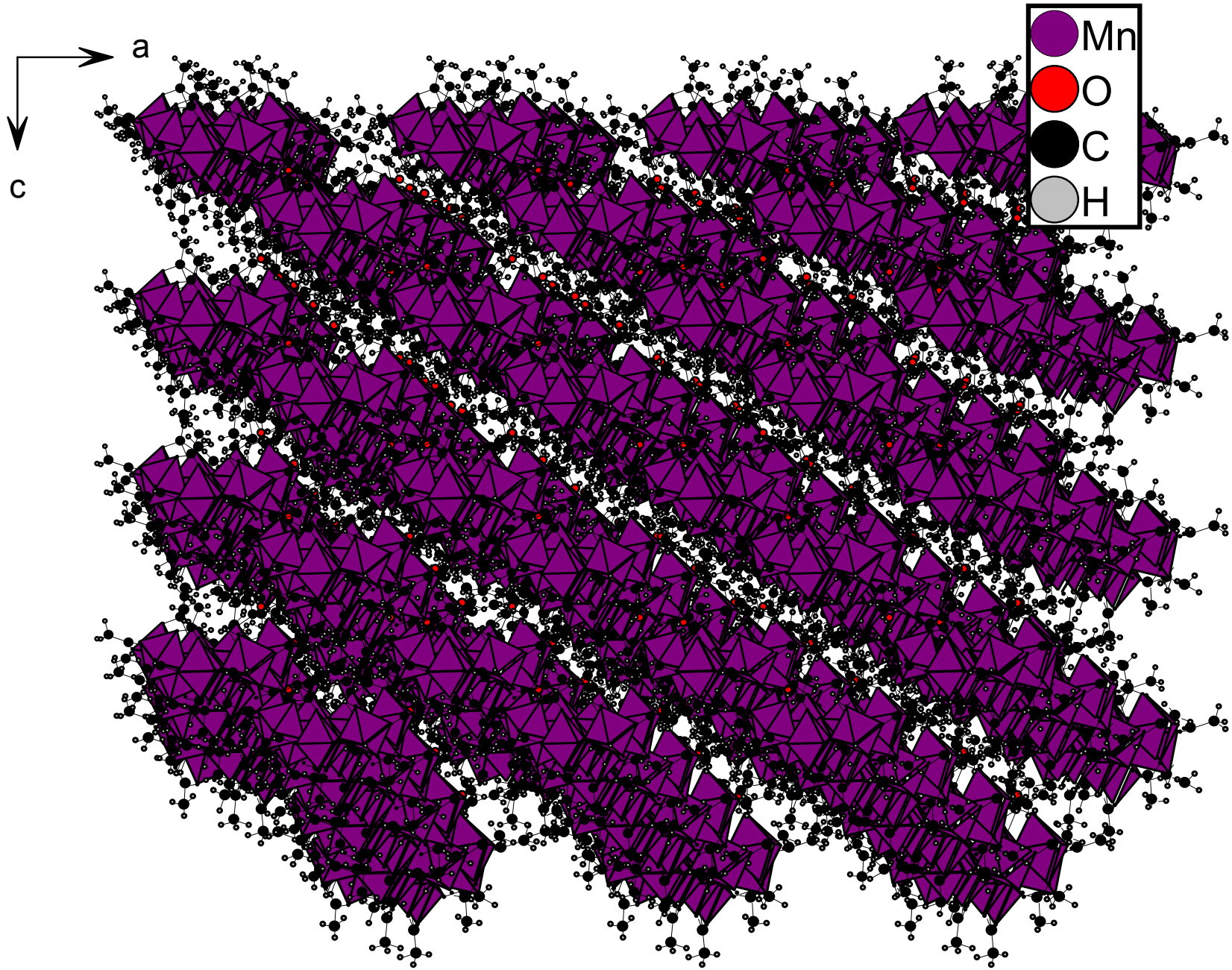
T = 125° C for 72 hrs

# Manganese Carboxylate Molecular Magnetic Clusters (R 1-12)

| Sample # | Salt | Salt (II) | Acid | Acid (II) | Water | Mixing Ratio |
|---|---|---|---|---|---|---|
| 1 | 4.001 g | 0.101 g | 2.5 ml | 0.165g | 1.8 ml | 1:0.5 |
| 2 | 4.00 g | 0.101 g | 2.5 ml | 0.331 g | 1.19 ml | 1:1 |
| 3 | 4.001 g | 0.100 g | 2.5 ml | 0.497 g | 1.81 ml | 1:1.5 |

| | Chemical Formula: | FW: |
|---|---|---|
| Salt: Manganese Acetate | $Mn(CH_3COO)_2$ X $4H_2O$ | 245.09 g/M |
| Salt (II): Potassium Permanganate | $KMnO_4$ | 158.03 g/M |
| Acid: 60% solution of Acetic Acid | $CH_3COOH$ | 43.23 g/M |
| Acid (II): Adipic Acid | $HO_2C(CH_2)_4CO_2H$ | 146.14 g/M |
| Water: Deionized Water | $H_2O$ | 18.00 g/M |

**Mixing Ratio** = Manganese Acetate: Adipic Acid  T = 60° C for 24 hrs


a
c
Mn
O
C
H

# Results:

## Note: all experimental runs have 3-samples per run

| Experimental Runs: | Date: | Comments: | Method |
|---|---|---|---|
| R 1-:<br>P#1 | 6-22-05 | Involved combining Iron (III) **Chloride Hexahydrate with Benzenetricarboxylic Acid** in order to produce an inorganic-organic hybrid framework. | Hydrothermal |
| R 1-2<br><br>P#2 | 6-24-05 | **Changed both salt and acid**: from Iron (III) Chloride Hexahydrate **to Manganese Acetate and** Benzenetricarboxylic Acid to **Succinic Acid** because of advice from advisor, Tony Cheetham. **Results :** all three samples were thrown out due to insufficient amounts of product. | Hydrothermal |
| *R 1-3<br><br>P#2 | 6-29-05 | **Changed salt,** from Manganese Acetate **to Manganese (II) Chloride** because of mentor's personal preference. **Now controlling** the value of **pH** by using Potassium Hydroxide. Sample **R 1-3-10: possibly Hausmannite (Mn3O4)** a type of Manganese Oxide from X-Pert high Score | Hydrothermal |
| *R 1-4<br>P#2 | 6-29-05 | **Same** mixing ratio as R 1-3, but **changed pH values** from: 12.5, 13, and 8.5 to **8.5, 10, and 13**. Samples **R 1-4-24, and R 1-4-26 both produced** combinations of **Hausmannite and Pyrolusite** from X-Pert High Score. | Hydrothermal |

| | | | |
|---|---|---|---|
| *R 1-5<br><br>P#2 | 6-29-05 | **Same** mixing ratio as R 1-4, but **changed pH values** from: 8.5, 10, and 13 **to 10, 8.5, and 13**. Samples **R 1-5-1, and R 1-5-3 both produced** combinations of **Hausmannite and Pyrolusite** (manganese oxide) from X-Pert High Score. | Solution Chemistry |
| Magnetic Clusters Sample #1<br><br>P#3 | 6-30-05 | Involved combining **Manganese Acetate, Acetic Acid, and Potassium Permanganate**. Note: burnt (voided) due to temperature sensitive compounds. | Solution Chemistry |
| R 1-6<br><br>P#2 | 7-5-05 | **Same** mixing ratio as R 1-5, but **changed pH values** from: 10, 8.5, and 13 to **8.5, 7.5, and 9.5**. **Note:** No possibilities from all three samples due to small peaks and large angles. | Solution Chemistry |
| *R 1-7<br><br>P#2 | 7-7-05 | **Same** mixing ratio as R 1-6, but **changed pH values** from: 8.5, 7.5, and 9.5 **to 9.5, 7, and 6**. **Sample R 1-7-24 produced a combination** of **Hausmannite ($Mn_3O_4$) and Rhodochrosite ($MnCO_3$).** | Solution Chemistry |

| | | | |
|---|---|---|---|
| Magnetic Clusters Sample #2 P#3 | 7-8-05 | Mixing ratios are the same as sample #1 (1:1), but **Added an Acid**, **Succinic acid** in order to link the clusters due to their bond lengths. Its color is black sludge. This **sample was not in the data base** and requires further investigation | Solution Chemistry |
| Magnetic Clusters Sample #3 P#3 | 7-8-05 | Mixing ratios are (1:0.25)<br>Manganese Acetate: Succinic acid<br>No results obtained (abort) | Solution Chemistry |
| Magnetic Clusters Sample #4 P#3 | 7-8-05 | Mixing ratios are (1:0.5)<br>Manganese Acetate: Succinic acid<br>No results obtained | Solution Chemistry: |
| R 1-8<br><br>P#2 | 7-11-05 | Involved **combining Cyclohexanol with Succinic acid and Manganese Chloride** in order to produce a Biphasic solution. To **produce crystals at the interface** between the acids and alcohol with the salt and water. No results obtained. | Solvothermal Synthesis |
| R 1-9<br><br>P#3 | 7-13-05 | Mixing ratios are: 1:1, 1: 0.75, and 1: 1.25<br>Manganese Acetate: Succinic acid<br>No results obtained | Solution Chemistry |

| | | | |
|---|---|---|---|
| R 1-10<br><br>P#3 | 7-13-05 | Same ratios as R 1-9 but done hydrothermally<br>No results obtained | Hydrothermal |
| R 1-11<br><br>P#3 | 7-15-05 | **Change in acid,** from Succinic Acid (4C) **to Adipic Acid (6C).** This is because Adipic is a longer carbon chain that we believe will allow for the bridging of the cluster. Mixing ratios: 1: 1.5, 1:1, and 1: 0.5<br>**Sample R 1-11-1** shows large chunks and under microscope appears to be **fin like crystals**. | Solution Chemistry |
| **R 1-12**<br><br>**P#3** | **7-15-05** | **Same mixing ratio and ingredients as sample R 1-11, but cooked at lower temperature. Sample R 1-12-3 shows large chunks and under microscope appears to be leaf/fin like crystals. Prep for x-ray, and compare powder pattern against Adipic Acid in database. Results show that our production is a re-crystallization of the Adipic Acid.** | **Solution Chemistry** |
| R 1-13<br><br>P#3 | 7-19-05 | **Same** mixing ratios and ingredients as sample R 1-12, **but hydrothermal**. **Results are unknown** due to filtering and preparation for x-ray powder diffraction required. | Hydrothermal |

| | | | |
|---|---|---|---|
| R 1-14<br><br>P#3 | 7-19-05 | **Same mixing ratios** as sample R 1-13, but **changed acid**, from Adipic acid **to Glutaric Acid (5C)**. **Results are unknown** due to filtering and preparation for x-ray powder diffraction required. | Solution Chemistry |
| R 1-15<br><br>P#3 | 7-20-05 | **Same mixing ratios** (1:0.5, 1:1, and 1: 1.5) as sample R 1-14, but cooked at a different temperature. **Results are unknown** due to filtering and preparation for x-ray powder diffraction required. | Solution Chemistry |
| R 1-16<br><br>P#3 | 7-20-05 | **Same mixing ratios** as sample R 1-15, but hydrothermal. **Results are unknown** due to filtering and preparation for x-ray powder diffraction required. | Hydrothermal |

**Challenges:**

-Producing a crystal worth doing a "single crystal diffraction" on (this would explain the structure of the crystal).

-Black Box Chemistry (we don't know how things are inside the autoclaves).

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-Learning Curve (learning a lot of new procedures in a short time).

Resources (retrieving supplies/equipment necessary for experiments).

-X-Ray Diffraction (scheduling availability and breakdowns).

**Problems:**

Both XRPD (diffractometers) have been inoperable at times.