Construction of a Holden Rotary Crystallizer

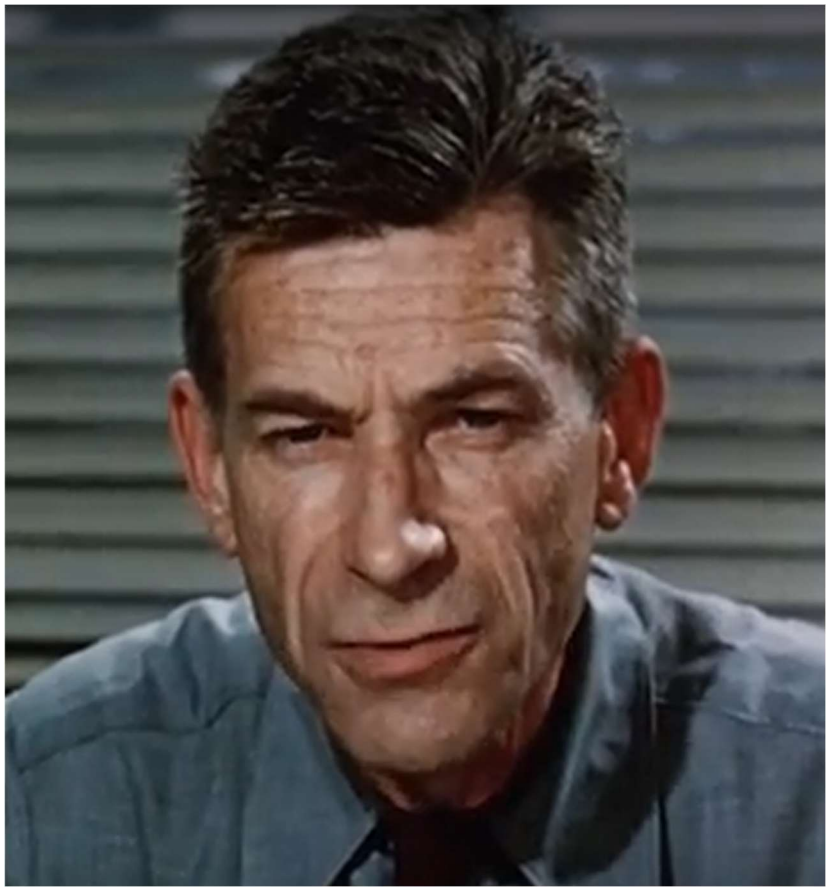
Holden Rotary Crystallizer, shown with Magnetic Stirrer and Inverse Solubility Base

Backstory:

- Back in 4th grade, I accepted an offer of after school "employment" in a mineral shop that I frequented. My "pay" was store credit, which kick-started a life-long fascination with minerals, especially crystals and fluorescents.
- The couple owning the mineral shop initially refused to let me purchase a book, "Crystals and Crystal Growing" (1960), by Alan Holden and Phylis Singer, explaining that it was "way over my head". I persevered, and devoured the entire book; I still have it, although it's falling apart.

- Over the next few years, I managed to make some decent alum octahedrons using the evaporation method. They had the usual veils and stray growths. I wanted to try to grow a chrome alum within a clear alum crystal, but I couldn't find chrome alum (being a kid).
- Fast forward to today: I wanted to revisit the crystal growing of my youth, but take things up a notch. Initially, I presumed that the evaporation method was still the method of choice.
- Those plans all changed after I did some searches on the book's lead author.

Alan Holden:



Alan Holden

- Alan Holden was a researcher at Western Electric (which subsequently became Bell Labs), where his primary activity during and after WWII was to develop improved methods for growing large, pure crystals of ADP (Ammonium Dihydrogen Phosphate). These piezoelectric crystals were required for wartime sonar transducers, where they rapidly replaced the older generation of sonar based on crystals of Rochelle salt (Potassium Sodium Tartrate Tetrahydrate).
- In his 1949 paper in Discussions of the Faraday Society, "Growing Single Crystals from Solution" (https://pubs.rsc.org/en/content/articlelanding/1949/df/df9490500312/unauth), Holden pointed out a number of downsides to traditional growth by evaporation, which led him to develop his rotary crystallizer. In that paper, he describes a 24 liter system, and mentions one that had a volume of 300 liters! The 1949 paper is available online, but I had to pay to download a copy.
- In 1960, Holden published the one and only lay press book devoted to this subject: "Crystals and Crystal Growing", with co-author Phylis Singer. This book was aimed at a general audience, and in the interest of simplicity, the recipes in the book only used the evaporation method.

- In 1964, Holden published a Bell Labs pamphlet entitled “Growing Crystals with a Rotary Crystallizer”. That was aimed at amateurs, and while the original pamphlet is no longer available, the good news is that it can be borrowed for free at the Internet Archive: https://archive.org/details/growingcrystalsw0000alan
- Holden published two books: “Conductors and Semiconductors, and “The Nature of Solids”. I’ve recently read both, and enjoy Holden’s writing style.
- He also made at least two videos at Western Electric / Bell Labs: “Crystals” in 1958, and another, “Matter Waves”, with Lester Germer in 1961. Germer was famous for the Davisson–Germer experiment that confirmed that electrons have wave properties. Both videos are on YouTube:
    - “Crystals”: www.youtube.com/watch?v=Wp6bN9vN6e4
    - “Matter Waves”: www.youtube.com/watch?v=szGJnpNowqw
- For all of his didactic skills, Alan Holden didn’t seem to cut it as a warm, caring father, as documented by one of his two sons (Jonathan): https://creativenonfiction.org/writing/imaginary-fathers. That piece includes a curious comment: “In the early ‘60s, Alan began constructing, with cardboard and Elmer’s Glue, three-dimensional, polyhedral models… By 1985, the polyhedra had almost entirely taken over the house”.

Phylis Singer/Morrison:

Phylis and Phillip Morrison

- Holden's co-author on their crystal growing book was Phylis Singer. Born Phyllis Hagen, she was a noted author and art/science educator. She collaborated on the video "Powers of Ten", as well as the PBS series "The Ring of Truth".
- When I wanted to get a new copy of my falling-apart "Crystals and Crystal Growing", I noticed that Phylis' last name had changed, to Morrison. That seemed familiar… Sure enough, she had married Phillip Morrison, the noted physicist.
- In the Jonathan Holden piece cited above, he mentions that Phillip Morrison was a regular visitor to the Holden household, and it strikes me as very likely that he met his wife there.
- Phillip Morrison worked under Robert Oppenheimer on the Manhattan project, and was subsequently an esteemed Professor of Physics at Cornell and then MIT.
- During my years at MIT, I saw him there regularly at the weekly Astrophysics colloquium. Having suffered polio as a child, by then he was wheelchair bound, and Phylis would always be there, lovingly wheeling him around the Institute.
- I once had the opportunity to dine with the Morrisons, but I had no clue at the time that his wife was the Phylis Singer who had co-written the book that I so enjoyed as a child. Had I known, I would have thanked her for co-authoring that influential book.

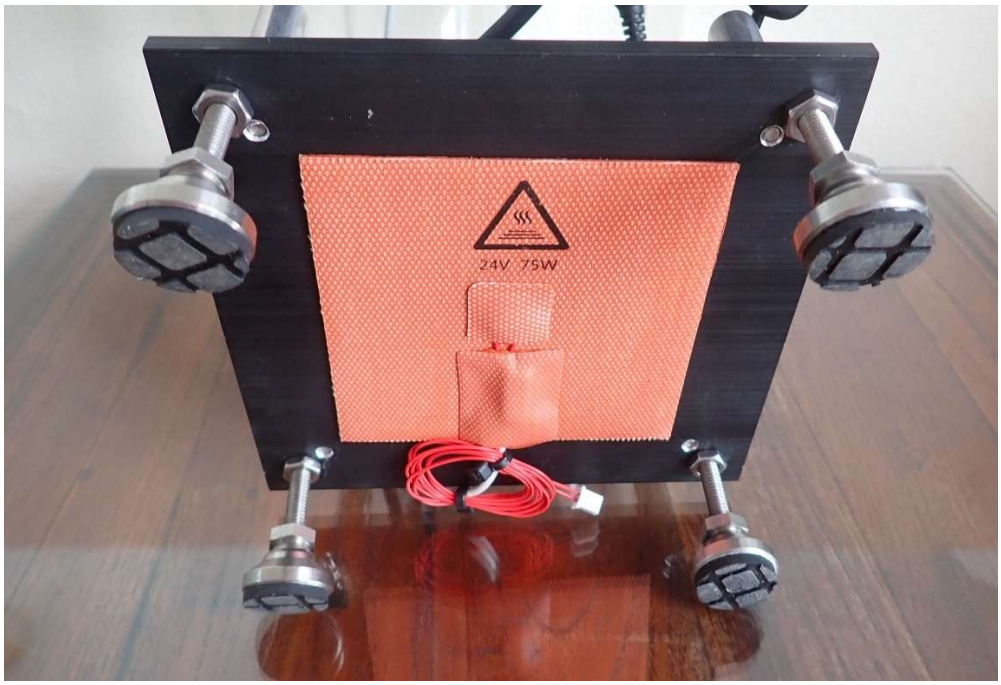
Alan Holden's Rotary Crystallizer Concept:

- While the evaporation method of crystal growing is very simple, requiring as little as a drinking glass, pencil, fishing line, and a suitable solution, it has a number of disadvantages, including:
    - Evaporation is usually too fast, and as the layers of atoms are laid down at high speed, veils and dislocations inevitably develop.
    - Evaporation supersaturates the surface of the solution, leading to crystals forming there, and falling on the primary crystal.
    - Dust reaching the surface serves as nucleation sites, producing yet more small falling crystals.
    - A significant portion of the solute crystallizes on the bottom of the container, often requiring transfers to a new, pristine growth vessel.
    - Variations in local solute adjacent to the crystal concentration deforms its faces.
- The rotary crystallizer solves all of these problems:
    - The container is sealed, so no dust can get in.
    - Saturation and crystal growth are controlled by precise temperature regulation, and at the typical temperature decrease of ~ 0.1°C per day, corresponding to a few hundred atomic layers per second, large transparent crystals of high quality can be grown. At this rate of temperature decrease, it can take 2-4 weeks to grow a suitably large crystal.
    - Evaporation from the surface condenses on the cooler lid of the sealed container and runs down the vessel walls, where the lower density pure water floats upon and dilutes the surface of the solution, preventing crystals from forming there.
    - The floor of the vessel is heated, which renders the solution near the floor under-saturated, prevent unwanted crystal growth there.
    - The seed crystal(s) are mounted on the ends of stainless steel rods extending radially from a central vertical shaft, which slowly rotates.

- The direction of rotation reverses every minute or so, preventing co-rotation of the solution, and avoiding concentration differences between the leading and trailing crystal faces. This reversing feature is omitted from the 1964 pamphlet, presumably to keep the mechanism simple, but is described as essential in the 1949 paper: "Unless the direction of rotation of the shaft is reversed at least once a minute, the solution rotates with the crystals and relative motion declines, and the crystals show veils on the "wake" side".
- Interestingly, what may well have been one of Holden's rotary crystallizers was recently found discarded by the side of the road, not far from the former Bell Labs location in Murry Hill, NJ: www.reddit.com/r/ChemicalEngineering/comments/1497fxu/diy_rotary_crystallizer_what_is_it_for_and_why
- With no microcontroller based PID temperature regulators available back then, precise control of the solution temperature was achieved using a "thermoregulator". This is basically a mercury thermometer, with the added twist of adding a precisely adjustable axial wire which contacts the conductive mercury as it rises when heated. The crystal growing vessel's heater (a light bulb) is turned on and off as the mercury level in the thermometer rises and falls. Pretty clever!

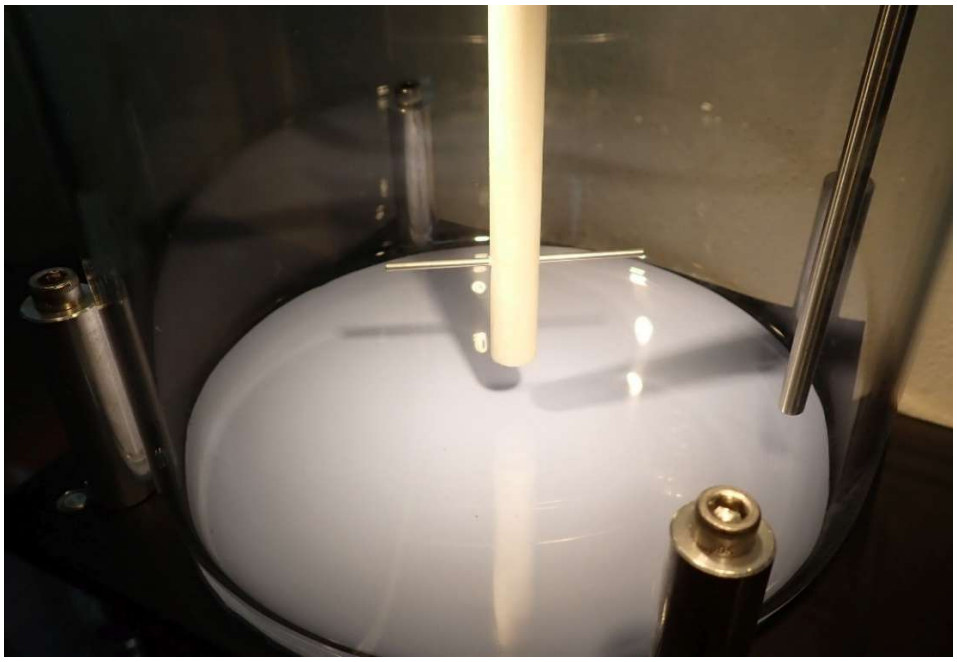
My Modern Version of the Holden Rotary Crystallizer:

- Some of the components used in the original rotary crystallizer, such as the mercury thermoregulator, are no longer made. The reciprocating motion back then was mechanically elaborate, and jerky. It was time to put a modern spin on things.
- The crystal growing vessel I chose is a very close match to the one suggested in Holden's 1964 pamphlet. It holds three liters, and is 150 mm OD by 200 mm high. I found it on Amazon for $21: www.amazon.com/Container-Canister-Airtight-Dispenser-Spaghetti/dp/B07TM8W6WB. It will be used with two liters of solution. Holden cautioned never to add hot liquids to the container, as the glass would break, but this product is low expansion borosilicate glass.
- Since the base of the growing vessel isn't perfectly flat, I poured thermally conductive epoxy on the base, and placed it on a layer of oiled saran wrap on a flat surface while the epoxy cured.
- The base is a black anodized 6" x 6" x ¼" aluminum plate, from McMaster-Carr: www.mcmaster.com/7083t31
- Rather than use a light bulb for heat, I adhered a 75 watt, 24 volt DC heating pad to the underside of the base plate: www.amazon.com/FYSETC-Printer-Voron0-1-Silicone-Heater/dp/B0D2Y2R4FL A layer of high temperature felt (not shown; www.mcmaster.com/8796k511) helps insulate the heating pad.



Underside of Crystallizer Base

- On the top of the plate, I adhered a circular pad cut from a compliant, thermally conducting mat: www.amazon.com/dp/B086VZ9YW3
- The base is supported by four adjustable pivoting feet, and four cylindrical spacers on the upper side help keep the crystal growing vessel centered on the base.
- The three-liter glass crystal growing vessel that I purchased included a bamboo lid with a snug fitting silicone gasket. I was concerned about the potential porosity of bamboo, and so I reverse engineered the lid and its gasket groove on a lathe, using a disc of high density polyethelyene (HDPE): www.mcmaster.com/8624k631
- A 3/8" diameter x 9" long polyester rod (www.mcmaster.com/7593t12) holds a pair of 0.065 diameter, 1" long 304 stainless steel tubes (made by cutting www.mcmaster.com/5560K73-5560K731 in half). Shallow holes are hand-drilled in a short axis face of the seed crystal(s), which are then bonded onto the rod ends using cyanoacrylate adhesive. The stainless steel tubes will later serve as the crystal's support for display purposes – no embedded fishing line to cut off.



Vertical Shaft and Seed Crystal Mounting Rods

- The vertical crystal growing rod penetrates the HDPE lid via a slip-fit, moisture resistant plastic flanged sleeve bearing (www.mcmaster.com/2705T22). A silicone film provides further moisture sealing.
- A pair of aluminum angle brackets form an open-on-the-sides electronic enclosure, which is fastened to the HDPE lid.
- The temperature sensor is a four wire RTD (100 ohm platinum; www.thermoworks.com/ths-160-446), which enters the growing chamber via a single-holed rubber stopper, and connects to the temperature controller. There were lower cost options, but a four wire RTD is the most accurate type, and I trust Thermoworks.
- An Omega CN16DPT-145 PID temperature controller (www.dwyeromega.com/en-us/1-32-1-16-and-1-8-din-universal-high-performance-controllers/CNPT-Series/p/CN16DPT-145) mounts to the front face of the enclosure, and features a 24 bit sigma-delta ADC and unlimited "ramp/soak" temperature vs time profiles. This was the most expensive component of the system; while low-cost Chinese temperature controllers are available, their documentation was poor, with ambiguous ADC resolution.
- The enclosure houses a 24 VDC, 5 amp power supply, as well as a 24 to 5 VDC converter, and a solid state relay.
- On the front face of the enclosure is an Arduino microcontroller (Pololu A-Star 32U4 Prime SV; www.pololu.com/product/3114), and a microstepping motor controller/driver that interfaces to the Arduino via I2C (Tic 36v4; www.pololu.com/product/3140).
- The vertical crystal support shaft is rotated by a 17 frame stepping motor (www.pololu.com/product/2267).
- The vertical crystal support shaft is bored and slit at its top to slip over the front shaft of the stepping motor, with a 3/8" clamp collar (www.mcmaster.com/6435k33) locking the shaft in place.

Rotary Crystallizer with Copper Sulfate Solution

- C code running in the Arduino microcontroller provides flexible control of the start speed, top speed, accel rate, and decel rate for the crystal support shaft. It was enormously helpful to be able to easily link in the Tic Stepper Motor Controller library for Arduino (https://github.com/pololu/tic-arduino). My C code is listed in Appendix A.
- The current program sets a microsteps per full step ratio of 256 (so 51,200 microsteps per revolution), a start speed of 3 rpm, a top speed of 10 rpm, and accel/decel times of 1 second. The motion profile consists of ten revolutions in each direction, with a pause between direction reversals of two seconds.
- A pair of high-intensity white LED micro spotlights (www.amazon.com/Taysing-Picture-Spotlight-Painting-Showcase/dp/B09WJ83D87) wired in series mount to the underside rear of the enclosure, and point down towards the growing crystal(s). These are

important for strongly colored solutions, where the growing crystal would otherwise be hard to see. Plus, who wouldn't want to light up their growing crystal!

- A fuse and on-off power switch are mounted on the rear face of the enclosure, along with jacks for the heater, cooler (see below), and LED spotlights.

Rear View of Electronic Enclosure

Separate Crystal Growing Vessel for Inverse Solubility Compounds:

- The system described above is ideal for growing crystals with normal compounds, whose solubility increases with increasing temperature. For these compounds, the net result of dissolving is endothermic (the solution cools when the solute is dissolved).
- But not all compounds behave that way. If the net result of dissolving is exothermic (the solution warms when the solute is dissolved), then the compound's solubility ***decreases*** with increasing temperature. This is referred to as "inverse solubility".
- Crystallizing compounds with inverse solubility requires a rethinking of how a rotary crystallizer should be configured. Fortunately, Holden's 1949 paper addresses this in its last few sentences: "The principles on which the apparatus described is based have been successfully embodied in a modification of the 4 liter apparatus for growing crystals of materials whose solubilities decrease with increasing temperature. The jar stands on three short legs in a shallow metal pan of water, with a constant-level attachment, so that the bottom of the jar is immersed to a depth of about ½", and is thus cooled. The heat input is distributed around a central zone by a fine Nichrome-wire winding on the jar, covered on the outside with felt. The crystals are grown in the zone immediately above the heated zone, and the temperature is, of course, progressively raised".

- I had already purchased some Neodymium Oxide, which I subsequently reacted with sulfuric acid to make Neodymium Sulfate. I only then realized that $Nd_2(SO_4)_3$ is one of those compounds whose solubility decreases with increasing temperature, so I needed to make a second crystal growing vessel and base to accommodate this.
- Solid-state Peltier coolers weren't available when Holden designed his rotary crystallizer, but they are readily available today, so I built a second crystallizer base with a Peltier cooler, heatsink, and fan on its underside (www.amazon.com/dp/B07ZCJT9V3), together with taller support feet to allow for sufficient airflow. The cooler assembly was designed to operate at 12 VDC, but since only modest cooling is needed to keep the floor free of crystals, and to lessen the power requirements for the nichrome heater, the Peltier cooler and fan work better at 5 VDC.

Peltier Cooler Assembly on the Underside of the Inverse Solubility Base

- The heater coil consists of a 3 meter ribbon of nichrome alloy, 3 mm wide x 0.2 mm thick (www.amazon.com/dp/B01HCB3VXC), wrapped just shy of eight times around the growth vessel, and secured with high-temperature 3M glass cloth tape: (www.amazon.com/dp/B004Z8YFCM). Nichrome is notoriously difficult to solder to, so I used crimp connections. The heating power at 24 VDC is about 100 watts, but this will be duty-cycle modulated by the PID temperature controller to deliver only the heating power that is needed.

Nichrome heating element, crimp connections, and glass cloth tape

- While a second growth vessel and base were required to support negative solubility vs temperature compounds, the lid and electronic assembly remain the same; all that is needed is to swap the lid and controller over to the alternate crystal growth vessel.
- As Holden points out in his 1949 paper, for these compounds, the temperature is slowly ***raised*** to grow the crystal.

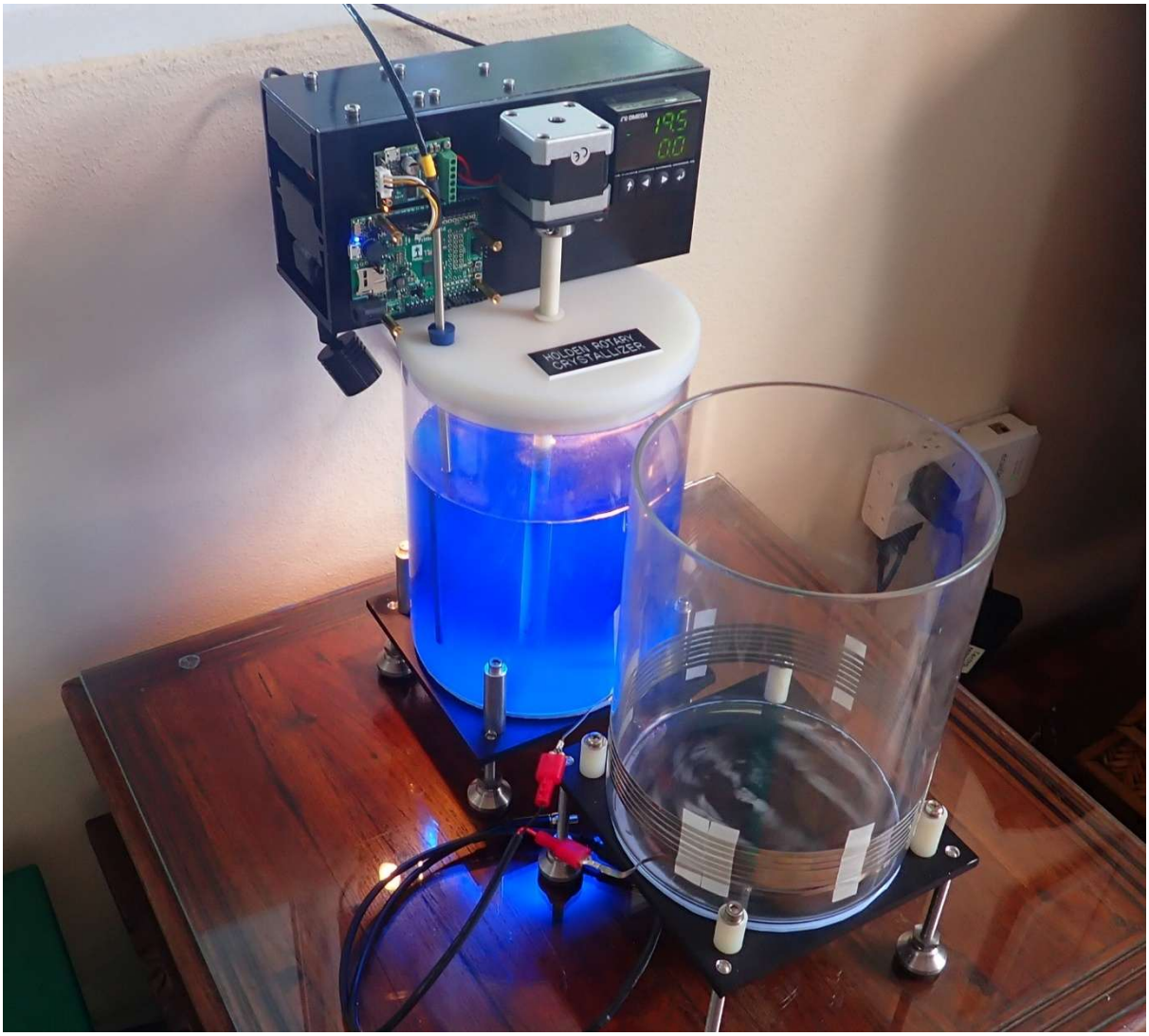
Now that the Holden Rotary Crystallizer is Complete:

I look forward to growing a number of crystals with the Holden Rotary Crystallizer, and have already acquired the following compounds:

- Copper Sulfate pentahydrate
- Potassium Aluminum Sulfate dodecahydrate (Alum)
- Potassium Chromium Sulfate dodecahydrate (Chrome alum)
- Neodymium Sulfate*
- Potassium Ferricyanide
- Potassium Sodium Ferrioxalate*
- Potassium Sodium Tartrate hexahydrate (Rochelle salt)
- Potassium Dichromate
- Ammonium Dihydrogen Phosphate (ADP)
- Potassium Dihydrogen Phosphate (KDP)
- Sodium Magnesium tris(Oxalato) Aluminum Chromium nonahydrate*

*Synthesized from precursors

I'm not tempted to scale up my Holden Rotary Crystallizer, but I found this comment in the "Handbook of Crystal Growth" interesting: "They [Zaitseva and colleagues at the Lawrence Livermore National Laboratories] demonstrated that the standard Holden crystallizer with temperature reduction could be used to grow large high-optical-quality KDP and deuterated KDP (DKDP) crystals **up to 50 cm on a side** at rates 10–100 times faster than older methods and without spontaneous nucleation and macroscopic defects". Incredible!



Holden Rotary Crystallizer with Inverse Solubility Base & Vessel

Here's a link to a video of the motion reversal of the Holden Rotary Crystallizer (no seed crystal mounted):
https://drive.google.com/file/d/1_MDfyJO9agBcn_zlzCOfz8qTejYx7x7s/view?usp=drive_link

Appendix A: C code listing for the Holden Rotary Crystallizer

This is available on Google drive as an Arduino sketch (.ino file), link below, but a text listing follows:

https://drive.google.com/file/d/1J8PN1GWm0LfOH48unrHwNPGV1cNWBBSG/view?usp=sharing

Text listing:

```
//Program to control the Holden Rotary Crystallizer

//Include the TIC stepper driver library

#include <Tic.h>
```

```
TicI2C tic;
void setup()
{
  // Set up I2C.
  Wire.begin();

  // Give the Tic some time to start up.
  delay(20);

  // Set the Tic's current position to 0, so that when we command
  // it to move later, it will move a predictable amount.
  tic.haltAndSetPosition(0);

  // Tells the Tic that it is OK to start driving the motor.  The
  // Tic's safe-start feature helps avoid unexpected, accidental
  // movement of the motor: if an error happens, the Tic will not
  // drive the motor again until it receives the Exit Safe Start
  // command.  The safe-start feature can be disbled in the Tic
  // Control Center.
  tic.exitSafeStart();
}

// Sends a "Reset command timeout" command to the Tic.  We must
// call this at least once per second, or else a command timeout
// error will happen.  The Tic's default command timeout period
// is 1000 ms, but it can be changed or disabled in the Tic
// Control Center.
void resetCommandTimeout()
{
```

```
  tic.resetCommandTimeout();
}

// Delays for the specified number of milliseconds while
// resetting the Tic's command timeout so that its movement does
// not get interrupted by errors.
void delayWhileResettingCommandTimeout(uint32_t ms)
{
  uint32_t start = millis();
  do
  {
    resetCommandTimeout();
  } while ((uint32_t)(millis() - start) <= ms);
}

// Polls the Tic, waiting for it to reach the specified target
// position.  Note that if the Tic detects an error, the Tic will
// probably go into safe-start mode and never reach its target
// position, so this function will loop infinitely.  If that
// happens, you will need to reset your Arduino.
void waitForPosition(int32_t targetPosition)
{
  do
  {
    resetCommandTimeout();
  } while (tic.getCurrentPosition() != targetPosition);
}

void loop()
```

```
{
  // Set Microstep Ratio, Start Speed, Max Velocity, and Max Acceleration
  tic.setStepMode(TicStepMode::Microstep256); // 256 microsteps per full step
  tic.setMaxSpeed(85333333);  // 10 rpm
  tic.setStartingSpeed(25600000);  // 3 rpm
  tic.setMaxAccel(298650);  // 1 second accel time
  tic.setMaxDecel(298650);  // 1 second decel time
  // Move to position 512000, which corresponds to ten counterclockwise revolutions of the crystal, and wait until it gets there.
  tic.setTargetPosition(512000);
  waitForPosition(512000);
  //Dwell at this position for two seconds
  delay(2000);
  //Move back to position zero, which corresponds to ten clockwise revolutions of the crystal, and wait until it gets there.
  tic.setTargetPosition(0);
  waitForPosition(0);
  //Dwell there for two seconds
  delay(2000);
  //and loop endlessly.  Temperature control is handled separately by the Omega CN16DPT-145.
}
```