Citrate-, and flux-methods for preparation of YBCO, $YBa_2Cu_3O_7$

In this exercise two exercises are run in parallel. $YBa_2Cu_3O_7$ is prepared in two different ways; powder is prepared by a citrate route and single crystals are made by flux growth.

The Material

$YBa_2Cu_3O_7$ was discovered in 1987 as the superconducting component in samples with bulk composition $Y_{1.2}Ba_{0.8}CuO_4$. this was the first known compound with a critical temperature (T_C) above 90K. This discovery accelerated the research into superconductors, both in attempts to prepare materials with higher critical temperature and in developing a theory for superconductivity. A great deal of effort is also put into development of application of the new high temperature superconductors. The high critical temperature made it possible to use liquid nitrogen as a coolant. This is much less expensive than liquid helium, which is in opractical use today, but there are still obstacles to be overcome before high temperature superconducting ceramic
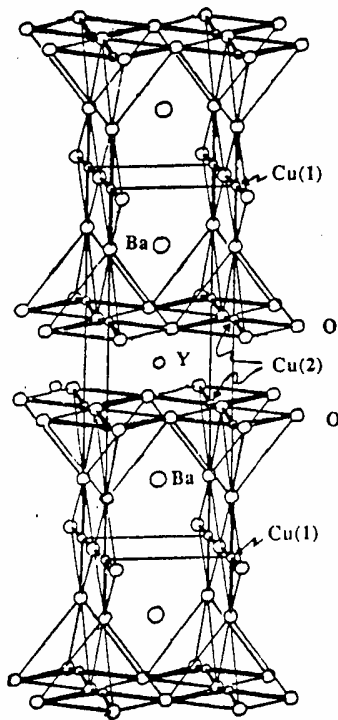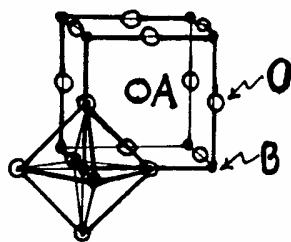
The crystal structure of the compound is shown in Figure 1a. It is orthorhombic and show similarities to the perovskite structure. Compared with the ideal perovskite structure this compound has ordered oxygen vacancies in the atomic arrangement. In addition, Y and Ba are ordered on A-type positions. This results in a tripling of the unit cell in the c-direction relative to the cubic perovskite. Cu, which is situated at the B-type positions, take two different coordinations, square planar for Cu_1 and square pyramidal for Cu_2. In the ideal perovskite structure all B-type cations are octahedrally coordinated. In $YBa_2Cu_3O_7$ copper has an

Fig. 1a Krystallstruktur for o-$YBa_2Cu_3O_7$

Fig. 1b Ideell perovskitt-type struktur

unusually high oxidation state (2.3) It is not possible to reach this high oxygen content except by annealing in oxygen at relatively low temperature.

The oxygen content may be varied between 7.00 and 6.35 for the orthorhombic $YBa_2Cu_3O_{7-\delta}$ phase. By further reduction a phase transition to a closely related tetragonal structure (composition $YBa_2Cu_3O_{6+\delta}$) occur. T_C decrease with decreasing oxygen content and is below 77K ($= T_{b,N_2}$) at 6.85.

Further development of the materials has increased T_C to around 160K.

The methods

The Citrate method is a type of sol-gel method, where the homogeneous atomic distribution in a liquid phase is attempted maintained by polymerization of citric acid complexes.

Citric acid is a tri-protonic carboxylic acid with the formula:

$$
\begin{array}{c}
H \\
H - C - COOH \\
H O - C - COOH \quad \bullet H_2O \\
H - C - COOH \\
H
\end{array}
$$
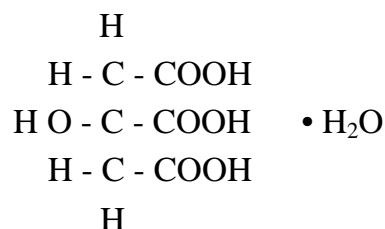
When different cations form complexes with the molten acid an intimate mixture of the ions on an atomic scale is obtained. During careful heat treatment in air of a solution of citric acid complexes polymerization and decomposition take place in parallel until a gel is formed. When the remaining water is removed from the gel a xerogel is obtained, which is an amorphous glass-like crust. Most of the organic content is removed by further heating of the the xerogel in air, usually at approx. 450C. the desired oxide is formed by heat treatment above the decomposition temperature of the carbonate.

Flux growth involves growth of crystals from non-aqueous solutions at temperatures above room temperature. The components of the desired product are dissolved in a solvent, the flux. Thereafter the product is precipitated in a process analogous to crystallization from aqueous solutions. As with growth from aqueous solutions, crystals grow at temperatures lower than the melting point of the material. This is especially important when: 1) the desired phase is incongruently melting, 2) a phase transition takes place to another (unwanted) modification before melting or 3) decomposition rather than melting takes place. Flux growth is also beneficial when the phase has a high vapour pressure at the melting point or if the melting point is very high.

A phase diagram for the solids present in the system Y-Ba-Cu-O at 900°C and 1 atm. O_2 is shown in Fig. 2. It is seen that $YBa_2Cu_3O_7$ (denoted 123 in Figs. 2 and 4) is in

equilibrium with CuO, Y_2BaCuO_5 (=211) and/or $BaCuO_2$, depending on the bulk composition of the sample. Closer studies have given the liquidus surface for the copper-rich part of the Y-Ba-Cu-O system as shown in Fig. 3. From this Figure it is seen which phases are obtained directly by cooling a melt with various compositions. We observe that only a relatively narrow composition-range will give $YBa_2Cu_3O_7$ as the primary precipitate. In order to obtain an impression of how the phase diagram looks in this area, a pseudo binary phase diagram for the section through the phases $YBa_2Cu_3O_7$ and Y_2BaCuO_5 is shown in Figure 4. This section is also indicated in Figures 2 and 3. We see that $YBa_2Cu_3O_7$ melts peritectically: $YBa_2Cu_3O_7 \rightarrow Y_2BaCuO_5$ + melt, and that a narrow compositional range exists (marked with a double arrow) where $YBa_2Cu_3O_7$ may be precipitated directly from the liquid phase.

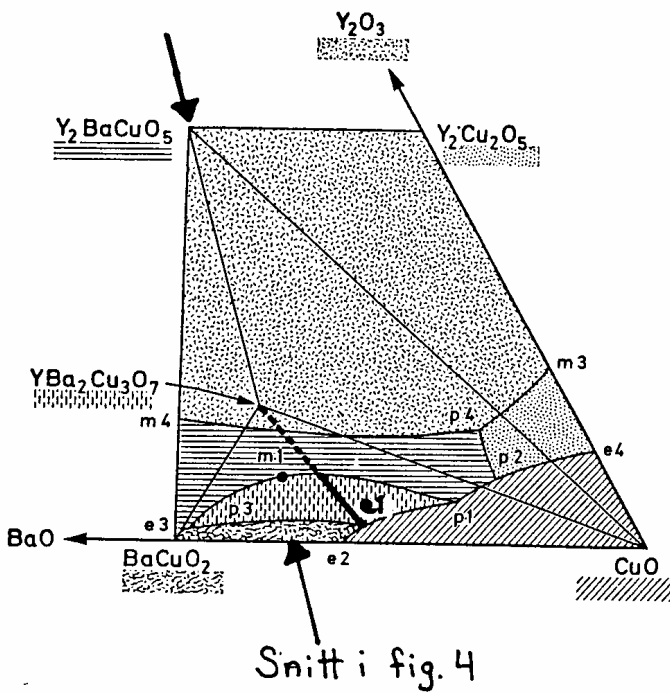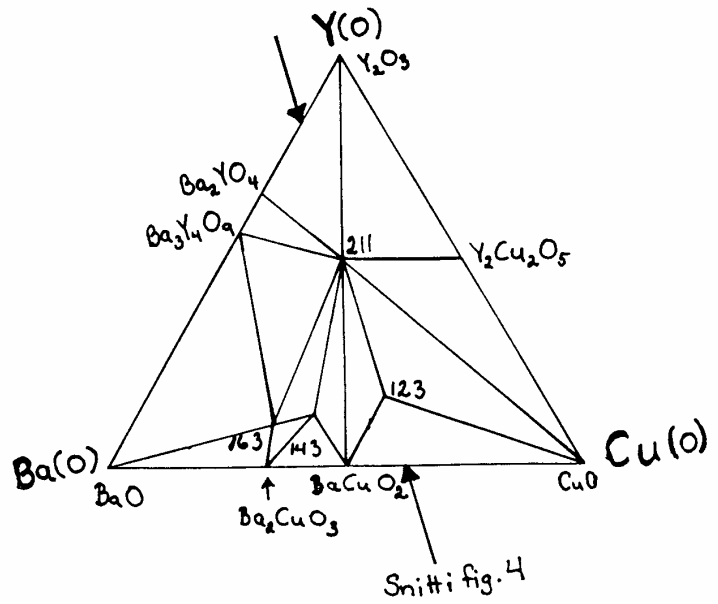**Figure 2:** Subsolidus phase diagram for the system: Y-Ba-Cu-O at 900°C and 1 atm O_2.

Y(O)

Y_2O_3

Ba_2YO_4

$Ba_3Y_4O_9$

211

$Y_2Cu_2O_5$

123

163   143

Ba(O)

BaO

Ba_2CuO_3

$BaCuO_2$

Cu(O)

CuO

Snitti fig. 4

Y_2O_3

Y_2BaCuO_5

$Y_2Cu_2O_5$

m3

$YBa_2Cu_3O_7$

m4

p4

p2

e4

m1

p2

BaO

e3

$BaCuO_2$

p1

e2

CuO

Snitti fig. 4

Figure 3: The liquidus surface for the Cu-rich part of the Y-Ba-Cu-O system.

t/°C

1100

900

Cu(O)

Y(O)   Ba(O)

$Y_2O_3 + L$

$Y_2O_3 + 211 + L$

211 + L

L

$123 + BaCuO_2 + L$

$123 + L$

$BaCuO_2 + L$

$BaCuO_2 + CuO + L$

$1/6 \ Y_5Ba(O)$

$(Y_2O_3 + BaY_2O_4)$

211

123

$1/8 \ Ba_3Cu_5(O)$

$(BaCuO_2 + CuO)$

123 felles fra
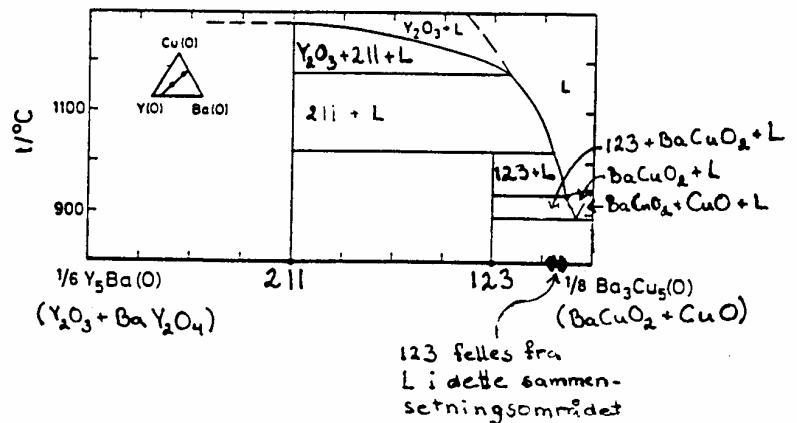L i dette sammen-
setningsområdet

Figure 4: A section through the Y-Ba-Cu-O phase diagram in air (P_{O2}=0,21 atm). L is the liquid phase

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Sections which are approximately parallell to the one shown, display similar regions of precipitation of $YBa_2Cu_3O_7$, with varying width and temperature range. The lowest temperature at which the flux is still liquid is at e1 (see Fig. 3); an eutectic where $YBa_2Cu_3O_7$, $BaCuO_2$ and CuO are in equilibrium with the liquid. This eutectic show similarities to the one found in the two-component system BaO-CuO, see Fig. 5, but it is shifted both regarding the compositional ratio between Ba and Cu and in temperature due to addition of Y_2O_3 and a different partial pressure of oxygen.
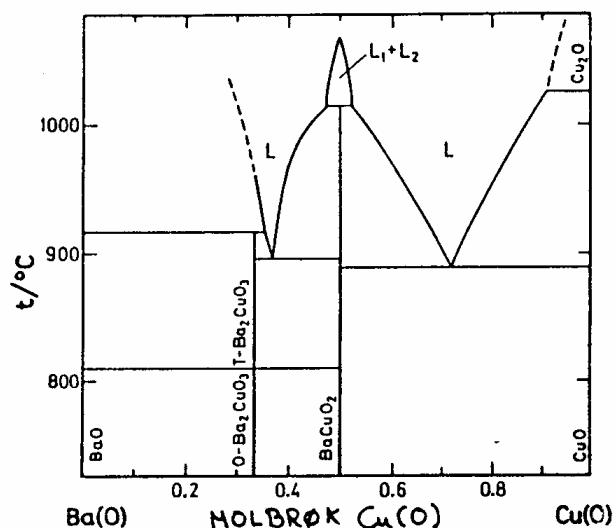

Fig. 5: The phase diagram for BaO-CuO in an Ar-O_2 mixture, P_{O_2} = 0,21 atm.

In order to obtain the largest possible yield of $YBa_2Cu_3O_7$, over a large temperature range, a bulk composition positioned on the full part of the line between $YBa_2Cu_3O_7$ and e1 should be used. When $YBa_2Cu_3O_7$ precipitates the composition of the melt is changed so that it at the end has a composition like the eutectic e1, where the lowest melting point in the Cu-rich part of the phase diagram is found. The cooling should be slow from a temperature above the peritectic for $YBa_2Cu_3O_7$ (1015°C) and down to a temperature somewhat above the eutectic (890°C). Further cooling will result in a mixture of $YBa_2Cu_3O_7$, $BaCuO_2$ og CuO.

No matter which synthesis method is used, the last step is a heat treatment of the $YBa_2Cu_3O_7$ samples in an oxygen rich atmosphere in order to achieve the desired oxygen stoichiometry. In this step the crystals made by the flux method will crack due to the strain from varying oxygen content (and thereby variations in the unit cell dimensions) through the crystal.

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The exercise

Starting ,materials:

- ✓ Y_2O_3 FW : 225,808 g/mol
- ✓ $BaCO_3$ FW : 197,35 g/mol
- ✓ CuO FW :   79,54 g/mol
- ✓ $CuCO_3 \cdot Cu(OH)_2 \cdot 0,5 H_2O$ FW : 230,11 g/mol
- ✓ Citric acid monohydrate

The starting materials may adsorb water and/or CO_2 from the atmosphere. This may lead to wrong assumption of the formula weight per cation compared to that given by the producer. All reagents are controlled regarding water and carbonate content, and the empirical formula weights given here are corrected (if needed) for the composition of the reagents.

Flux growth:

Procedure:

Weigh Y_2O_3, CuO og $BaCO_3$ so that the total composition of the sample is: 6.25 mol % Y, 29.77 mol % Ba og 63.98 mol-% Cu. ($BaCO_3$ decomposes to BaO by heating.) Start by weighing carefully ca. 1 g Y_2O_3. Your calculations must be approved before mixing the three ingredients in a mortar and press them into pellets.

See Figure 6 for use of the pellet press. Do not use excessive force when pressing- it should be possible to remove the pellet from the equipment without destroying it. The press equipment is cleaned using 96% ethanol. The piston should be moved up and down in the cylinder in order to remove traces of solids from the walls.

NB! DO NOT USE WATER OR ACID TO CLEAN THE PRESS EQUIPMENT. KEEP THE EQUIPMENT CLEAR OF PA\LACES WHERE HCl IS USED

Fig. 6: Pellet press.
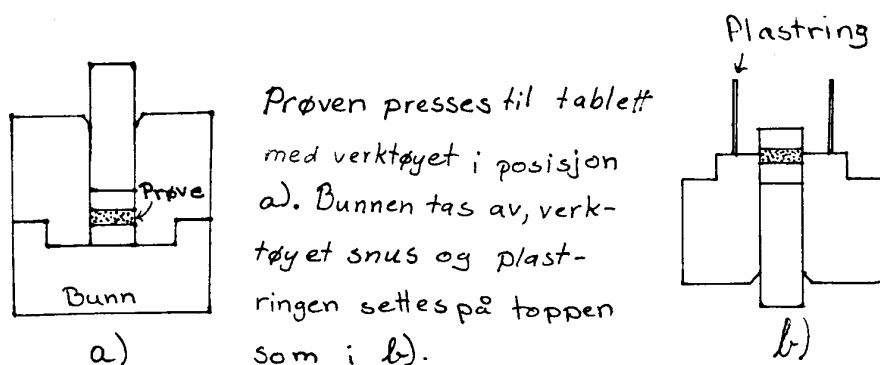
Load the pellets in an alumina crucible so that the samples have the least possible contact with the walls of the crucible. Put some pellets close in the bottom of the crucible, then build a tower of pellets on top, so that the upper pellets are not in contact with the walls of the crucible. The crucible is placed on a MgO plate, which is situated in a quartz glass boat and placed in the furnace. Put an extra quartz boat into the furnace at the same time. Program the furnace with the temperature profile you have been provided with by the laboratory responsible (see the manual for the temperature regulator). Different heating profiles may be tried during the course, and the results should be compared at the end of the laboratory course in order to determine the best synthesis conditions with respect to cooling rate and end temperature.
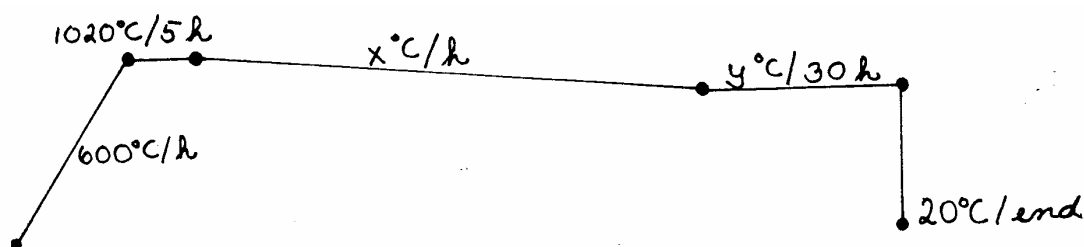

Fig. 7: Temperature profile for flux growth of $YBa_2Cu_3O_7$.

When the temperature has reached Y°C the flux is poured quickly into the extra quartz boat, see Figure 8. In order to get rid of the flux residues, the crucible is place upside-down on the MgO plate and the furnace is closed.

DURING THESE OPERATIONS YOU MUST USE THE WELDING MASK AND HEAT RESISTANT GLOVES. POURING OF THE FLUX MUST ONLY BE DONE WITH THE LABORATORY RESPONSIBLE PRESENT.

Because the pouring of the flux must be done quickly, you should practice using the tongs and protection gear at room temperature before pouring the flux from the actual sample in the furnace.

The next day the crucible is removed from the furnace. The crucible is put right-side-up and placed on a hest resistant plate to cool.

The crystals are loosened from the walls of the crucible. Look at them in the microscope, estimate the size, and pick some for later heat treatment in the furnace with oxygen stream together with the samples prepared by the citrate method.

It is a good idea to start preparing the citrate method samples while the flux-sample is in the furnace.
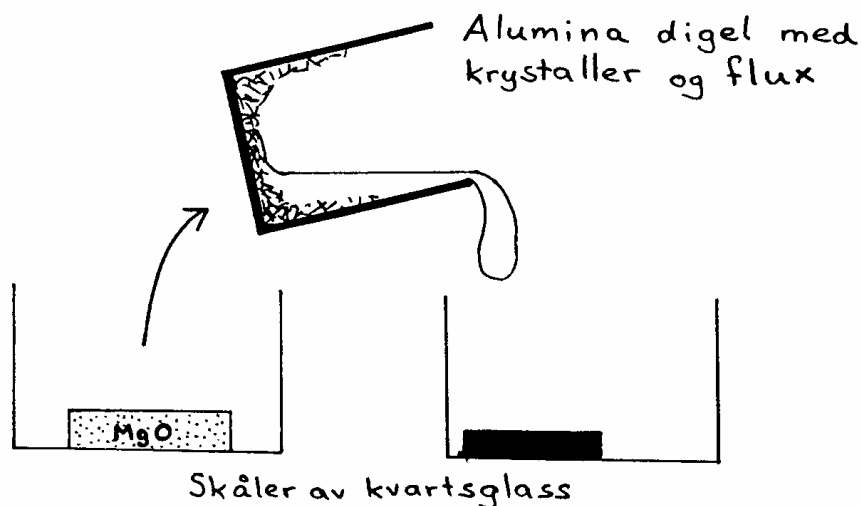
Fig. 8: Pouring of the flux.

The citrate method:

Procedure:

Weigh approximately 25g citric acid in a 150 ml beaker. Put in the bar magnet for a magnetic stirrer. Weigh carefully ca. 0.5 g Y_2O_3 and put it into the beaker. Citric acid and yttrium oxide is stirred at room temperature with a watch glass as lid in order to avoid dust. In the mean time stoichiometric amounts of $BaCO_3$ and $CuCO_3 \cdot Cu(OH)_2 \cdot 0.5 H_2O$ (ca. 1.8 and 1.5g, respectively) is weighed.

The citric acid (with Y_2O_3) is melted quickly under stirring on a hot plate which in advance has been turned on at maximum temperature. It may be useful to introduce a very small amount (a few drops) of distilled water in order to avoid local decomposition of the citric acid. Because Y_2O_3, due to kinetics, is difficult to dissolve in dilute solutions of citric acid it is important not to add too much water at this point. When the acid is completely melted the beaker is put on a hot plate which has been set at 180C in order to complete dissolution of Y_2O_3. It is necessary to this low temperature in order to avoid too early decomposition of the citric acid. (Decomposition is detected as a yellow colouring of the melt.

When Y_2O_3 is completely dissolved, $BaCO_3$ is added gradually. It is important to add only a small amount at a time in order to limit the evolution of CO_2 gas. It is necessary to avoid spill over due to froth formation in the beaker. Use distilled water to rinse the last of the powder from the container used for weighing into the beaker, so that everything is introduced into the mixture. (Contrary to Y_2O_3, $BaCO_3$ and $CuCO_3 \cdot Cu(OH)_2 \cdot 0.5 H_2O$ are easily dissolved in dilute citric acid.)

The basic copper carbonate is added little by little. Again froth is formed due to carbon dioxide formation. Use distilled water to add the last of the powder into the beaker. The solution is then diluted with didtilled water to a total volume of ca. 50 ml. Depending on the degree of dilution the liquid will vary strongly in viscosity (from black currant syrup to honey like). In some cases a "mother of pearl"-like appearance is obtained. This is probably caused by polymerization and does usually not influence the process. The xerogel will be amorphous anyway.

When all starting compounds are dissolved, the solution is transferred to a porcelain bowl. This is covered by aluminium foil and put into a laboratory furnace at 180ºC to decompose over night.

The next day the sample is removed from the furnace. It should now be a brown porous crust. The crust is easily crushed using a pistil and the bowl is put into a muffle furnace at 450ºC for two hours or until the mixture no longer glows when the door to the furnace is opened. In this step most of the organic part is burned off.

After cooling the sample is pressed into one or several pellets as described in the flux-synthesis part. The pellet(s) are put into an alumina boat.

The porcelain bowl is first washed with water and then put into a 1:1 solution of HCl for 15 minutes in order to dissolve the residues. Finally it is washed with water.

Annealing and sintering:

The alumina boat contaning the pellets is placed in a furnace, heated to 900C and left at that temperature over night.

Turn off the furnace and let the boat stand in the furnace until it is no longer red-hot before taking out the alumina boat. Cool the samples in air. Crush each pellet in a mortar (cover with a plastic bag to minimize loss of the product). After the preliminary crushing the samples should be transferred into the ball mill containers. The balls are introduced and acetone is added up to ca 1 cm below the rim of the container. Ball mill the samples for 5 minutes.

> *When using the ball mill both containers must by places in the mill and the weight must be approximately equal. This means that two samples must be run simultaneously. It is possible to run one of the containers only with balls and acetone, but this should be avoided as it is wearing out on the balls and container*

When the ball milling is completed the containers are removed from the mill, the lids are removed and the containers are placed in a fume hood until the acetone has evaporated.

When yhe acetone has evaporated the samples are pressed into pellets and placed in a furnace with oxygen flow for the final heat treatment. Remember to include the crystals from the flux growth in this treatment.

Procedure for using the furnace:

1.   Put in the sample.
2.   Close the ends of the alumina tubes with the end-plugs.
3.   Turn on the cooling water.
4.   Program the temperature regulator with the following temperature profile:
       (Refer to the manual for the unit)

900°C/20 h

2°C/min

5°C/min

370°C/16 h

10°C/min
20°C/end
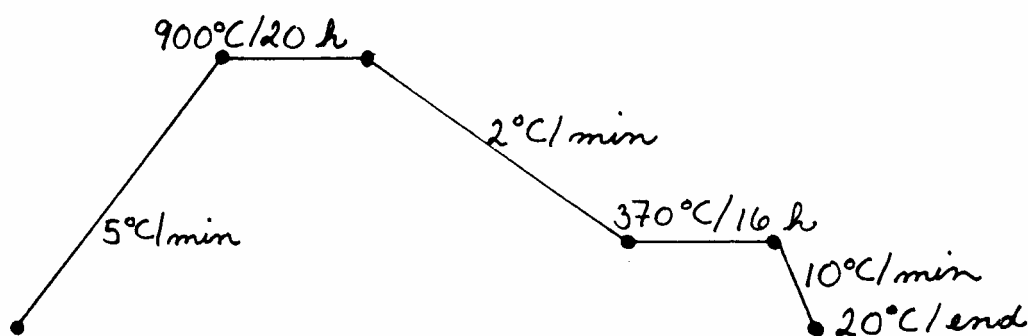
5.   Sett he oxygen flow to 2 l_n/h. refer to the calibration curve for the flow meter. Directions for using the reduction valve is posted at the oxygen cylinder.
6.   Start the temperature program.

After this heat treatment the samples are finished and ready for testing with respect to phase purity, crystal structure, oxygen content, superconducting properties etc. results from characterization of previous samples will be distributed.
The alumina boat is put into 1:1 HCl : water for cleaning. It is then rinsed with water and dried in a laboratory furnace at 180C.

Questions for the report:

Characterization:

On one of the lab benches there are a Dewar with liquid nitrogen and a megnet. Test the superconductivity of your samples by putting the magnet on top of the cold sample and see if any levitation is observed.
As mentioned earlier, you should compare the size of your flux grown crystals with other made at slightly different synthesis conditions, and attempt to find the most

suitable conditions for flux growth of large crystals. Remember to give the approximate size of the crystals in the report.

Comment on the differences between citrate and the flux growth method.

Comment:

Whwn preparing single crystals of $YBa_2Cu_3O_7$ by flux growth it is observed that the unit cell parameters are not identical to those for samples prepared using different methods. This is especially trus for samples prepared in alumina crucibles and is caused by attack of the flux on the crucible. This results in Al3+ being released into the melt, and these ions are incorporated in $YBa_2Cu_3O_7$. Research has shown aluminium contents up to $YBa_2Cu_{2.874(8)}Al_{0.10(1)}O_{6.31}$. (The low oxygen content is obtained because the sample was analyzed before the final heat treatment in oxygen.)

This illustrates one of the problems with flux growth. At the high temperatures the flux is chemically aggressive and it is difficult to find suitable materials for the crucible. Furthermore, there is a larger tendency to incorporate contaminants into the single crystals.