Synthesis of high temperature superconductor using citrate pyrolysis and observing the Meissner effect

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Superconductor materials conduct electricity with precisely zero resistance. High critical tememerature (Tc) superconductors have considerable potential for technological applications ranging from generation and transmission of electric power to digital electronic devices. Superconductors have the ability to carry more than hundred times the amount of current than ordinary aluminum or copper wires of the same size. This experiment presents a techniques for synthesizing yttrium barium copper oxide (YBCO) superconductors, with the chemical formula $YBa_2Cu_3O_7$. This material is famous among high Tc superconductors and has attained considerable interest in the past two decades. It was the very first material to superconduct above the boiling point of liquid nitrogen. High Tc superconductors are usually synthesized using solid-state reactions at extremely high temperatures. This paper documents an alternate technique for obtaining high purity products in relatively less time, the defining process being citrate pyrolysis.

KEYWORDS

Superconductors · Solid State Reaction · Citrate Pyrolysis · Meissner Effect · Diamagnetism · Annealing

Approximate Performance Time 2-3 weeks.

References and Essential Reading

[1] D.H.A. Blank, H.Kruidhof, J.Flokstra, J. Phys. D: Appl. Physics. **21**, 226-227 (1988).

[2] J.R. Hook and H.E. Hall, *Solid State Physics* , Second Edition, pp. 278-290 (1991).

[3] Stephen Blundell, *Magnetism in condensed matter*, Oxford University Press, 198-217 (2001).

1 Theoretical background

Superconductivity was discovered by H. Kammerlingh Onnes while he was investigating the electrical resistance of metals near absolute zero temperature. He noticed that some materials underwent an abrupt drop in resistance, down all the way to zero, at characteristic temperatures, now known as transition temperatures denoted by Tc (Fig. 1). Materials which showed this property were called superconductors. At first, most materials exhibited this property at liquid helium temperatures (4.2-7.2 K), but then newer materials, most of them oxides, were discovered with very high transition temperatures in the range 35-100 K. These are now known as high temperature or high-Tc superconductors [2].
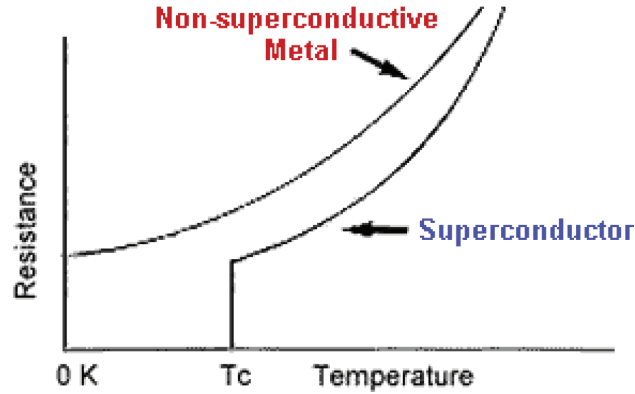

Figure 1: R Vs T graph of a typical superconductor.

2 Magnetic properties of superconductors

Superconductors, regardless of their transition temperature, may be classified using their magnetic properties (Fig. 2). Type I Superconductors have a single critical magnetic field (let us call that H_c). If any field stronger than H_c is applied, a type I superconductor will lose its superconducting behavior and the flux will completely penetrate the solid. For fields applied up to H_c however, the type I superconductor completely excludes the field from its bulk, thus making it a perfect diamagnet with magnetic susceptibility $\chi = -1$ [3].

Type II Superconductors have two critical fields, let's call them H_{c1} and H_{c2}. When a magnetic field is applied on a superconductor with strength lower than H_{c1}, the superconductor expels the magnetic flux from its bulk completely. However, when a magnetic field with strength between H_{c2} and H_{c1} is applied, there is partial flux penetration in the superconductor, and yet the superconductor still retains its zero resistance property. When a magnetic field is applied with strength greater than H_{c2}, there is a breakdown of superconductivity and the flux is completely excluded from the solid. High Tc Superconductors are type II Superconductors with relatively high H_{c2} fields [2].

The superconductor that we will synthesize in this experiment is called the YBCO superconductor (yttrium barium copper oxide), chemically represented as $YBa_2Cu_3O_{7-\delta}$, and it is more colloquially referred as a 1-2-3 superconductor due to the ratio of metal atoms in its chemical formula. The quality of the final superconducting prod-
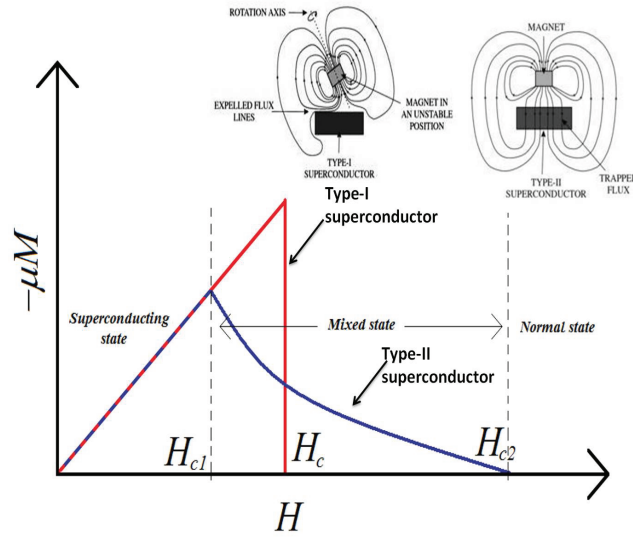
Figure 2: Magnetization curves of Type I and Type II superconductors.

uct is dependent on the oxygen content of the molecule. It has been experimentally determined that YBCO's crystal structure undergoes a radical change when y approaches 6.4. First, the symmetry changes from tetragonal to orthorhombic, and second, the material undergoes a transition from an insulator state to a metal state [2]. Furthermore, as y increases from this point to 6.9, the critical temperature goes up to 92 K, as opposed to 40 K when $y = 6.4$ [2]. It will therefore be our goal, to oxidize the material as much as possible using various types of heat treatments that will be discussed further.

3 Brief introduction to citrate pyrolysis

The citrate pyrolysis method was first discovered in 1987 and was proven to be more reliable than the typical solid state reaction as the obtained powder in citrate pyrolysis is ultra-fine and bears the correct stoichiometric values, whereas the powder obtained by the series of solid-state reaction is prone to developing impurities [1]. Furthermore, the citrate pyrolysis method yields the product faster as compared to the typical solid-state reaction. This paper documents a partially modified technique (than the one documented in 1987), based on the research findings of an experiment performed in the LUMS SBASSE Physics Laboratory during the summers of 2013.

Q 1. What is magnetic susceptibility, and perfect diamagnetism?

Q 2. How can you distinguish between a paramagnet, diamagnet, and ferromagnet?

Q 3. What is superconductivity? Define persistent current?

Q 4. What is critical magnetic field and critical temperature of a superconductor?

Q 5. Why is ferromagnetism lost on heating in a ferromagnet?

4   List of chemicals and equipments

Yttrium oxide (Y_2O_3), barium nitrate [$Ba(NO_3)_2$], copper nitrate [$Cu(NO_3)_2.3H_2O$], citric acid ($C_6H_8O_7$), nitric acid (HNO_3), de-ionized water, acetone, pyrex beakers, fume hood, magnetic stirrer and hot plate, spatula, mass balance, filter paper, aluminum foil, mortar and passel, ceramic crucibles, muffle furnace, Pellet dye, hydraulic press (also called pellet carver machine), liquid nitrogen

5   Experimental procedure

In this experiment, we will synthesize a 1-2-3 superconductor using a so-called citrate pyrolysis method and verify its superconductive state through its diamagnetic behavior.

Before handling any chemicals, wear latex examination gloves and lab coat. Also use safety goggles when handling a hot solution.

1. Fill a 1 Liter pyrex beaker with about 50 mL of deionized water. Place this beaker inside a ventilated fume hood and on a magnetic stirrer. Do not place the ceramic pellet into the beaker yet.

2. Keeping in mind that we wish to maintain a stoichiometric ratio of 1:2:3 of Y:Ba:Cu (refer to detailed calculations given in the appendix), we first measure 1 g of Y_2O_3 on a high sensitivity mass balance using a spatula. It is advisable to use aluminum foil rather than filter paper to measure Y_2O_3, in order to reduce the chance of impurity contamination. Furthermore, one should be careful to clean the spatula with acetone after every use. Transfer the Y_2O_3 to the beaker containing the deionized water. At the end of this step, turn on the suction mechanism of the ventilated cabinet.

3. You will now have a milky white solution. Carefully heat the solution on the magnetic stirrer at about 50-60 °C (while again taking care of cleaning the magnetic ceramic pellet before using it. Use a moderate stirring speed. Slowly add dilute nitric acid using a pipette until the solution turns transparent. This dissolves Y_2O_3 which is insoluble in water.

4. Proceed to measure 3.063 g of $Ba(NO_3)_2$ and 8.981 g of $Cu(NO_3)_2.3H_2O$ and transfer it to the beaker, leave the beaker on the magnetic stirrer, while all the powder dissolves. You will now have a clear blue solution.

5. Measure 5.533 g of citric acid $C_6H_8O_7$ and transfer it to the beaker. We usually use a 2:1 ratio of metal nitrates to citric acid.

   Before proceeding on to the next step, make sure all of your chemicals have dissolved in the beaker, and that there are no noticeable residues or precipitates. If there are any, then your solution may have been contaminated by impurities.

6. While keeping the magnetic stirrer on, turn the heating knob of the stirrer to about 100°C, and close the hood of the ventilated cabinet. It is important to note that the temperature on the knob is not the same as the temperature

of the solution. Further, it is imperative that we do not use a thermometer to avoid the risk of impurity contamination, and also that a thermometer might shatter in the spontaneous combustion reaction. Hence, the goal of this step is to heat the solution such that it does not come to a boil, while allowing it to evaporate.

7. Using a visual estimate, when 11-15 mL of the solution is left, turn off the stirring mechanism and turn up the heating knob of the magnetic stirrer to a maximum. Maintain a safe distance from the apparatus after performing this step, wait and observe.

8. The solution should now spontaneously combust (this happens due to the presence of nitrates), providing the basis for the pyrolysis reaction. When the entirety of the solution is consumed, turn off the heating knob.

9. Collect the obtained powder (which should be brownish black) in a ceramic cup using a spatula.

10. Heat the obtained powder in a furnace (Brother furnace XD-1200N) while using the heating curve shown in Fig. 3, while keeping the powder inside the ceramic cup. This step is intended to anneal the sample (for 2 hours at 900°C, thereby increasing the ductility of the substance. The furnace should return to room temperature in about 24 hours after it has been turned on. It is important that we do not try to accelerate or perturb the cooling phase of any kind of heat treatment as it might create irregularities in the crystal structure of the compound which are vital in achieving superconductivity. (Fig. 3)

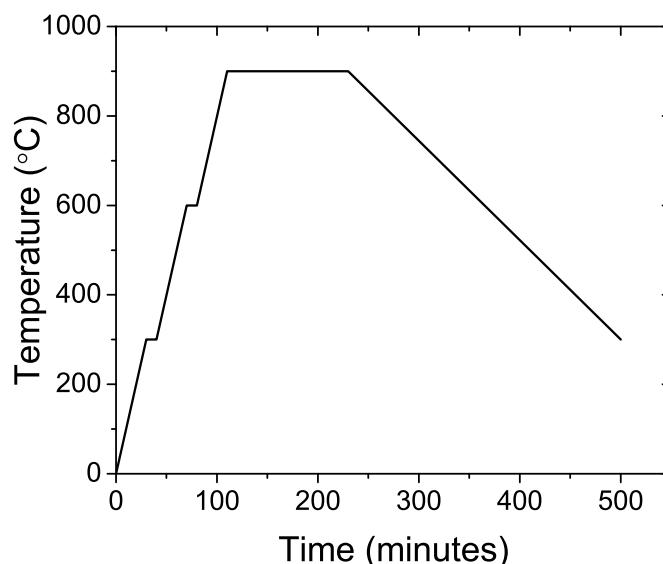Question: Read up on annealing, its purpose and how it is different from sintering?

Figure 3: Heat treatment profile - Note intervals of 10 minutes at 300 and 600°C, parallel line for 2 hours heat treatment at 900°C and rightmost descent of temperature.

11. After the furnace returns to room temperature (or close to it, around 40-50 ^oC), we may take out the ceramic cup containing the powder, which should now be a strong black. Next, grind the powder in a grinding bowl to obtain fine particles.

12. Collect the fine powder in a ceramic cup and proceed to make pellets (preferably two or three, depending upon the amount of powder obtained). Detailed instructions on making pellets are given below.

Procedure for pellet formation

(a) From left to right (Fig. 4), we have (A, B) two pellet caps (one has its flat side up, the other has its round side up), (C) the rod, (D) the mould, (E) the holder, and (F) the base.
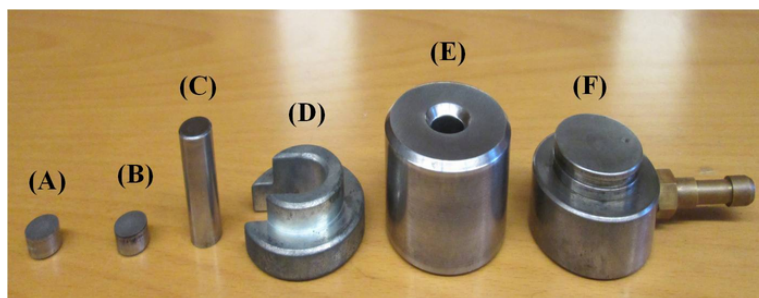

Figure 4: Different parts of the dye.

(b) Place the mould over the base, insert one of the pellet caps (with the flat side up, this is very important!) into the hole. The arrangement of the dye parts can be seen in Fig. 5.
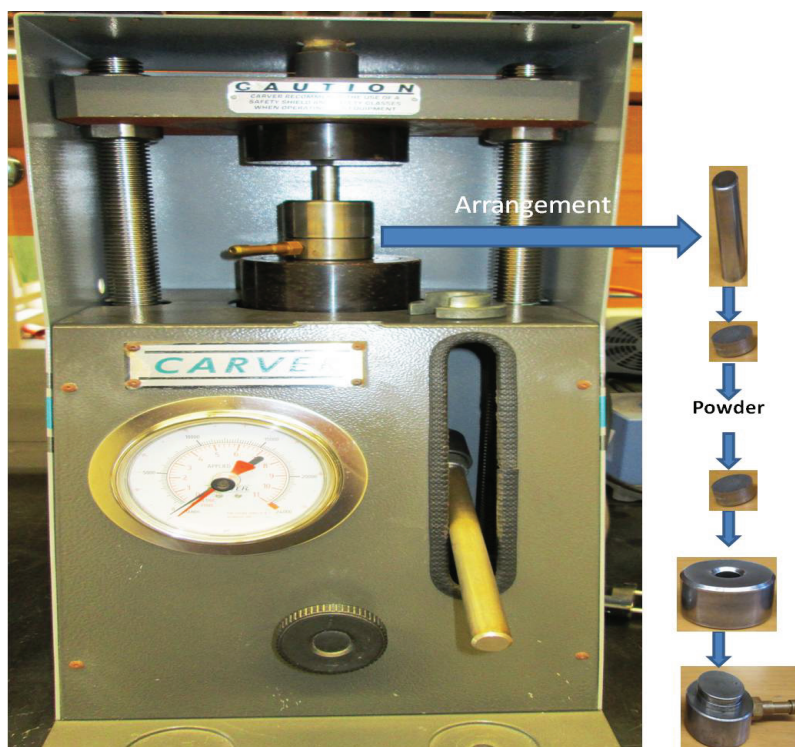

Figure 5: Hydraulic press and arrangement of dye parts for pellet making.

(c) Using a spatula, place approximately 1.25 g of fine powder into the hole containing the pellet cap.

(d) Insert the second pellet cap into the hole, this time with its flat side down.

(e) Insert the rod into the hole (flat side faced down) until it completely sinks down. It is important that the rod is perpendicular to the mould.

(f) Now move onto the pellet carver machine, turn the knob below the dial anti-clockwise to relieve pressure first, and then turn it clockwise to lock it. Place the entire mould structure into the pellet carver, rod faced up, and then close the protective shield.

(g) Finally, using the rod, pump the pellet carver up until the rod meets the carver ceiling, then pump it to 7 tons, or 15000 pounds on the dial. Leave it to that much for 3 minutes.

(h) Using the knob, relieve the pressure on the structure, and take the structure out.

(i) Remove the base, turn the structure upside down (while holding the rod), and insert the holder into the previous position of the base. Insert the structure into the pellet carver, this time with the rod facing down.

(j) Lock the carver pressure knob and the protective shield, and pump the machine until the pellet caps pop out in front of the holder.

(k) You will find your pellet in between the pellet caps, you may repeat the process to make more pellets. Be careful in handling the pellets for they are quite delicate at this stage.

13. Place the pellets in ceramic cups, and re-heat them in a furnace using the heating curve described in Step 10. This time, the heat treatment would be classified as sintering, a treatment that is intended to increase the compactness and workability of the pellet.

14. After sintering, place the pellets in an evacuated tube and heat them for 24 hours in flowing oxygen in a tube furnace, in accordance to the heating curve given below in Fig. 6 (900°C for 24 hours), This heat treatment, is purely intended to increase the oxygen content of the compound. We would like to bring the stoichiometric ratio of oxygen as close to 7 as is possible.

15. You may now finally test your superconducting pellet. In a styrofoam cup, place a small magnet (preferable 2.5×2.5mm) on top of your pellet. It is advisable to cut your cup such that it's total height is around 6 cm. This way you'll be able to handle the pellet more easily. Also, keep plastic tweezers in hand. Pour liquid nitrogen in the cup (while wearing insulating gloves!) such that the pellet is completely submerged in liquid nitrogen. Further, if the magnet falls off, you may use your plastic tweezers to place it back on top of the pellet.

16. There should be considerable boiling around the pellet, and finally, when the boiling stops, you should be able to see your magnet either strongly repelled by the pellet, or, if you've placed it close to the center of the pellet, levitate.

17. If your pellet had no effect on the magnet whatsoever, it may be possible that it is still underdoped in oxygen. In that case, it is advisable to repeat
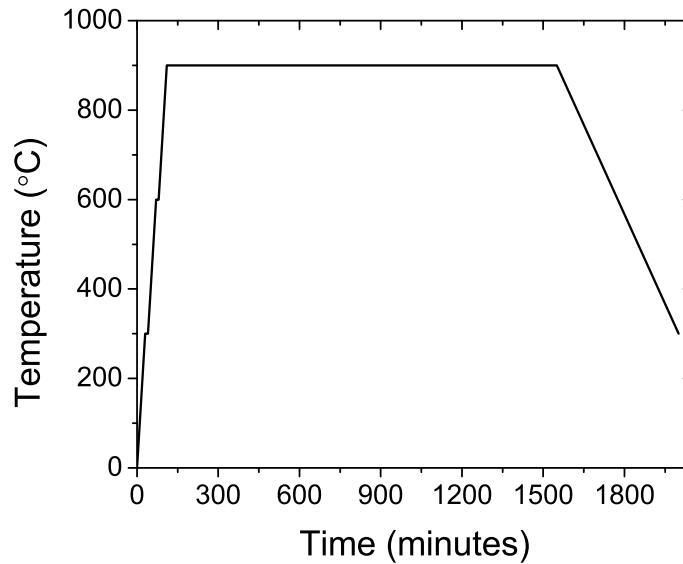
Figure 6: Second heat treatment profile - Note intervals of 10 minutes at 300 and 600°C, parallel line for 24 hours heat treatment at 900°C and rightmost descent of temperature.

steps 14 through 16 while keeping the same pellet. Even if you could see considerable levitation as in Fig. 7, it would still be advisable to repeat steps 14 through 16 just to ensure maximum oxidation.
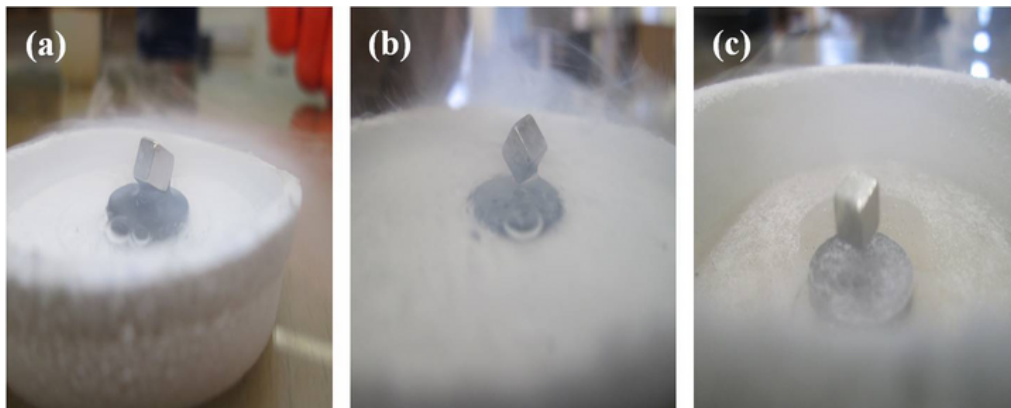

Figure 7: Meissner effect showing levitation for (a) one (b)two and (c) eight heat treatments.

Q 6. What is Meissner's effect?

Q 7. The Meissner effect allows a magnet to float above a superconductor (or vice versa). Can you think of any potential applications using this effect?

6 Further Considerations

1. If an oxygen environment is unavailable, step 14 may also be carried out in a normal muffle furnace. However, the final product may be underdoped

Table 1: Molar masses of chemicals

Chemical	Molar mass	Chemical	Molar mass
Y (Yttrium)	88.906	$Y(NO_3)_3.6H_2O$	478.894
Ba (Barium)	137.33	$Ba(NO_3)_2$	261.34
Cu (Copper)	63.546	$Cu(NO_3)_2.3H_2O$	241.6
Y_2O_3(Yttrium Oxide)	225.809	$C_6H_8O_7$	192.124

in oxygen. Research experiments in the LUMS Physics Laboratory have shown however, that when step 14 is carried out in a normal furnace, the final sample exhibits superconductivity around liquid nitrogen temperatures (although the levitation was not as much as that of the sample prepared in an oxygen environment). Even so, repeated heat treatments in normal furnaces may yield results that are very close to the quality of superconducting YBCO that is achieved through heat treatments in oxygen.

2. If we wish to obtain a stoichiometric ratio of Y:Ba:Cu of 1:2:3 using Y_2O_3, $Cu(NO_3)_2.3H_2O$ and $Ba(NO_3)_2$, then the principle ratio to be used is 1 : 3.063 : 8.981 corresponding to Y_2O_3:$Ba(NO_3)_2$:$Cu(NO_3)_2.3H_2O$. The amount of Citric Acid used should be adjusted while using $Y(NO_3)_3.6H_2O$ as an estimate instead of Y_2O_3, as the standard for deciding the amount of citric acid is generally with respect to metal nitrates used. You may refer to detailed calculations given at the end of the manual.

7 Appendix

First note the respective molar masses of the elements and compounds. Note that we need a molar mass ratio of Y:Ba:Cu of 1:2:3. Hence let us assume that we started with 3 g of Y_2O_3. First, let us find the amount of yttrium that contains.

$$\text{Mass of Y in } Y_2O_3 = \frac{\text{Total M}_r \text{ of Y in } Y_2O_3}{\text{M}_r \text{ of } Y_2O_3} \times \text{Mass of } Y_2O_3 \text{ used} \qquad (1)$$

$$\frac{88.906 \times 2}{225.809} \times 3 = 2.3623\, g \qquad (2)$$

Q 8. Following the formula and mass requirement of Ba and Cu. Find the required masses of $Ba(NO_3)_2$ and $Cu(NO_3)_2.3H_2O$?

Q 9. Note down the resolution of the mass balance and clearly mention the practical masses you have measured?

It is verified that there is 2.3623 g of Y in 3 g of Y_2O_3 correspond to a required ratio of 2.3623:4.7246:7.0869 in grams of Y:Ba:Cu; and to achieve this, we therefore require a final ratio of 3:9.19:26.94 in grams of Y_2O_3:$Ba(NO_3)_2$:$Cu(NO_3)_2.3H_2O$. This can be simplified to 1:3.063:8.981 in grams, which is the principle ratio used in this experiment.

We now proceed to calculate the required amount of Citric Acid ($C_6H_8O_7$) for this reaction mixture. The experimental standard is to use a 2:1 ratio of metal

nitrates to fueling agent (which in this case is citric acid). Therefore, we will use an approximation, we will assume that we used yttrium nitrate ($Y(NO_3)_3.6H_2O$) instead of yttrium oxide, and hence use the number of moles for yttrium nitrate that correspond to the amount of yttrium in 1g of yttrium oxide (as that is what we used). From Equation 5, we find that in 1 g of Y_2O_3, we have 0.7874 g of Y. So we will now find the corresponding amount (and moles) of $Y(NO_3)_3.6H_2O$ that will yield 0.7874 g of Y.

$$\frac{\text{Total M}_r \text{ of Y in Y(NO}_3)_3.6H_2O}{\text{M}_r \text{ of Y(NO}_3)_3.6H_2O} \times \text{Mass of Y(NO}_3)_3.6H_2O \text{ used} \qquad (3)$$

$$= \text{Mass of Y in Y(NO}_3)_3.6H_2O \qquad (4)$$

Substituting values we now have,

$$\frac{88.906}{478.894} \times \text{Mass of Y(NO}_3)_3.6H_2O \text{ used} = 0.7874g \qquad (5)$$

This gives us the analogous amount of $Y(NO_3)_3.6H_2O$ to be 4.24 g. Hence, we now have a ratio of $Y(NO_3)_3.6H_2O$:$Ba(NO_3)_2$:$Cu(NO_3)_2.3H_2O$, which is 4.24:3.063:8.98 in grams.

Using the following formula, we can calculate the number of moles of each of the chemicals we have used;

$$\frac{\text{Total Mass Used}}{\text{Mass Number of Compound}} = \text{Number of moles} \qquad (6)$$

You will find that we have used 0.008537 moles of $Y(NO_3)_3.6H_2O$, 0.01172 moles of $Ba(NO_3)_2$, and 0.0371 moles of $Cu(NO_3)_2.3H_2O$. Hence, the total number of moles of metal nitrates is simply $0.008537 + 0.1172 + 0.0371 = 0.0576$. Note that 0.0576 moles of Citric Acid corresponds to $0.0576 \times 194.124 = 11.060$ g of citric acid. Furthermore, since we are using a 2:1 ratio of metal nitrates to fueling agent, we will require $11.060/2 = 5.533$ g of citric acid. Make sure you go through all of these steps and a clear working is shown in your notebook.