Synthesis of a High Temperature Superconductor

In this laboratory exercise we will synthesize the ceramic YBa$_2$Cu$_3$O$_{7-x}$, called the 1-2-3 Superconductor because of its metal's stoichiometry. The importance of this material is that it is a high temperature superconductor of Type II. As such, a pellet of this material, when immersed in liquid Nitrogen, will exhibit the Meissner effect by levitating a small magnet.

Superconductivity is a property whereby a material loses all resistance to the flow of electrons within it. Hence, a current, once started in a superconductor, will continue to flow indefinitely. This property was first discovered by Heike Kamerlingh Onnes in 1911 when he observed the resistance of a column of Mercury dropped to zero when cooled to about 4K.

In the spring of 1911, Onnes began his studies of electrical conductivity of metals at low temperature. Physicists at the time knew that resistance generally dropped as a sample was cooled, but they had no idea what happened when the temperature reached the extreme lows near absolute zero. Some had hypothesized that resistance would continue dropping slowly, finally reaching zero when the temperature reached zero. Others believed resistance would level off at some constant value. Still others, including Lord Kelvin, believed that near absolute zero electrons would essentially freeze into place and resistance would become infinite. Onnes intended to resolve the question.

Believing that any impurities in a metal would spoil his results, Onnes chose mercury for his studies because he could produce extremely pure samples of the metal. He had been working with gold at the time as well, but selected mercury instead, a fortunate choice, since had he stuck with gold he would not have discovered superconductivity.

Keeping the mercury in a U-shaped tube with wires at both ends,
he passed a current through it and measured resistance as he lowered the temperature. At first, as the temperature dropped, the resistance also dropped slowly. Then, suddenly, at 4.19 Kelvin, the resistance abruptly vanished. Onnes was shocked. This was not what anyone had predicted.

At first Onnes didn’t believe what he saw; he thought perhaps there was a short circuit or some other problem with the apparatus. He and his team repeated the experiment until finally Onnes became convinced that the surprising effect was indeed real. In late April 1911, he published his first paper, titled “The resistance of pure mercury at helium temperatures” in the Communications from the Physical Laboratory at Leiden. He published a second paper in May, and in November 1911, Onnes published another paper entitled “On the Sudden Change in the Rate at which Resistance of Mercury Disappears.”

Soon after finding the effect in mercury, Onnes showed that tin and lead also become superconducting at low temperatures.

As Onnes observed, superconductivity sets-in when the material is cooled below a critical temperature $T_c$, the point at which an abrupt phase transition causes the material's resistivity to drop to zero.

![Resistivity vs Temperature Graph](image)

For metals such as Mercury, Tin and Lead, $T_c$ is typically well below 20K. Alloys of Niobium exhibit some of the highest values of $T_c$ for this class of superconductors; Nb$_2$Ge is the current record holder with a $T_c$ of 23.3K. In 1986, another class of superconductors was discovered which have $T_c$ values that can exceed 100K. Unlike previously known superconductors, these materials, typically Copper containing Oxides, are ceramics.

The first of this second class of superconductors discovered was La$_2$CuO$_4$ with a $T_c$ equal to 35K. Because it was observed $T_c$ tended to increase with pressure, attempts were made to decrease the lattice spacing of this material by substituting smaller cations for the La$^{3+}$; for example, Yttrium (cation radius = 104 pm) for Lanthanum (cation radius = 117 pm). This paid-off as YBa$_2$Cu$_3$O$_{7-x}$, the 1-2-3 superconductor, was found to have a $T_c = 92K$. The big advantage this material has over other superconductors is that it can be cooled to superconducting temperatures with liquid Nitrogen, boiling point 77K.

When cooled below $T_c$, Type I superconductors, typically elemental metals that exhibit superconductivity, exhibit what is called the Meissner effect, discovered by Walther Meissner.
and Robert Oschenfeld in 1933, whereby the material, when placed in an external magnetic field $\mathbf{B}$, experiences no internal magnetic field. The magnetic field is excluded from the interior of the material. This causes the external field lines to "bulge" slightly around the material. 

Type II superconductors, typically compound superconductors, at certain temperatures, allow the external magnetic field lines to penetrate their interior slightly. When a small magnet is placed above a Type II superconductor, it appears to be levitated (see above). This is because the magnetic field from the small permanent magnet will induce a supercurrent to flow within the superconductor. This supercurrent will induce a magnetic field with poles opposite that of the external magnet. This will establish a repulsive force that can be sufficient to overcome the downward force of gravity. Type II superconductivity is required because the slight penetration of the external magnetic field provides for a resistance that damps lateral motion of the small magnet.

The unit cell for our 1-2-3 Superconductor is an orthorhombic structure formed by stacking Perovskite ($\text{CaTiO}_3$) like structures.
Superconductivity is thought to be associated with CuO$_2$ sheets within the unit cell. These sheets are connected by CuO$_3$ chains that are required because they provide additional electron density to the CuO$_2$ sheets.

Finally, we turn to the synthesis of our high temperature superconductor. There are a couple of methods commonly employed for its synthesis. The method we will use involves mixing the oxides of each metal in stoichiometric proportions and heating them until the reaction is complete. The heating stage is critical. We initially heat the mixture to 930°C. During this heating period the basic structure of the Superconductor is established by diffusion of the appropriate ions. The material is then cooled to 500°C where further reaction occurs with Oxygen in the Air to provide a net deficit of about $x = 0.1$ in the final formulation of YBa$_2$Cu$_3$O$_{7-x}$. This process can be represented roughly as:

$$\frac{1}{2} \, \text{Y}_2\text{O}_3(s) + 2 \, \text{BaO}_2(s) + 3 \, \text{CuO}(s) \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_{7-x}(s)$$

Once our compound has been synthesized, we will test it for its ability to levitate a small magnet when cooled to liquid Nitrogen temperatures.
Procedure


1. Weigh out 0.60g of Yttrium Oxide (Y2O3) and place it in a small beaker. Add stoichiometrically correct amounts of Barium Peroxide (BaO2) and Cupric Oxide (CuO).

2. In a fume hood, transfer your powdered mixture to a mortar. With a pestle mix and grind the material for about 10 minutes. Use a spatula to scrape material from the sides of the mortar to prevent it from caking there. Your final powder should be uniform in color with no white or black spots apparent.

   **All these chemicals are toxic. Avoid creating or breathing dust when grinding. Avoid eye and skin contact.**

3. Scrape the powder onto two creased pieces of weighing paper; dividing your sample into two.

4. Use a pellet press to press each of your samples into pellets. (If the pellet crumbles as it is ejected from the press, re-press it again.)

5. Place each pellet into an Alundum Boat for heating.

6. Heat the pellets in a furnace that is raised to 930°C over a period of 8-12 hours. Then hold the temperature of the furnace at 930°C for 12-16 hours.

7. Allow the furnace to cool to 500°C and hold it there for 12-16 hours. Then turn off the furnace and allow it to cool to room temperature.

8. Remove the pellets from the furnace. They should dark grey or black. A dark green material is a non-superconducting material Y2BaCuO5.

9. Store the cooled pellets in a desiccator.

10. When ready, use plastic forceps to transfer the pellets to a cut-off styrofoam coffee cup. Place a small magnet on top the pellet. Pour liquid Nitrogen from another cup into this one until the pellet is fully covered with the Nitrogen. Add more Nitrogen to keep the pellet covered, as needed. Observe the magnet. Touch it gently with your forceps and it should begin to spin as it levitates.

11. Use the "solids" model kit to build the following two models:

   - Perovskite
   - 1-2-3 Superconductor (modify the Perovskite directions as needed)
Post-Lab Questions

1. Based on your model building exercise:
   a) What is the coordination number of the Ca, Ti and O for Perovskite?
   b) Explicitly show that the unit cell for Perovskite corresponds to a formula of CaTiO$_3$.
   c) Explicitly show that the unit cell for 1-2-3 Superconductor corresponds to the correct chemical formula.

2. What are the oxidation states of Ca and Ti in Perovskite? Are these normal?

3. Consider the Yttrium, Barium and Oxygen in the 1-2-3 Superconductor to have the following oxidation states: Y$^{3+}$, Ba$^{2+}$ and O$^{2-}$. Based on this, what fraction of the Copper has an oxidation state of Cu$^{2+}$ and what fraction is Cu$^{3+}$?

4. Why did we have to compress our powdered material into pellets prior to placing them into the furnace?

5. What is the current record for a "high-temperature" superconductor?

6. What does it imply about the Copper atoms that the 1-2-3 Superconductor has a chemical formula of YBa$_2$Cu$_3$O$_{7-x}$ with $0.0 < x < 0.4$?

7. Identify the CuO$_2$ sheets and CuO$_3$ chains in the unit cell of the 1-2-3 Superconductor.
References

http://hyperphysics.phy-astr.gsu.edu/hbase/solids/maglev.html

http://www.aps.org/publications/apsnews/200704/history.cfm

