Perfecting a Super-recipe: A Study of Pb-doped Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{11-\delta}$ Superconductors

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Introduction to Superconductivity. When physicist Heike Kamerlingh Onnes, from the Leiden University of Netherlands, first liquefied helium on July 10, 1908, he “opened an entirely new chapter in low-temperature physics” (van Delft and Kes 2010). Upon opening the possibility of obtaining a temperature reading for metals at a nearly 0 Kelvin (K), the absolute lowest physical temperature at which all electron movements subside, Kamerlingh Onnes introduced the world to superconductivity.

Superconductivity is “the characteristic pertaining to certain metals, compounds and alloys in which their resistivity becomes zero” when placed in frigid temperatures (Giancoli). Resistivity is the amount or measure of “resistance” or “opposition” to permit electric flow, known as electrical current, in a material. A useful analogy to picture this characteristic is to compare “the flow of electric charge in a wire to the flow of water in a river, or in a pipe, acted on by gravity. If the river or pipe is nearly level, the flow rate (current) is small”, but if one end is somewhat higher than the other, the electric current is greater (Giancoli). Continuing with this analogy, the walls of a pipe, or the banks of a river and rocks in the middle, offer resistance to the water current.

These low temperature superconductors (LTS) possess two prominent, exceptional characteristics that set them apart from other materials:

1. They experience no internal resistance, allowing for “persistent currents” to be contained in the presence of an applied current. Without resistance, superconductors do not follow the correlation of internal current represented as a flowing river. Instead, they resemble a nearly endless waterfall, with nothing opposing its current flow of descent. This lack of resistivity permits a current to continually flow within the material. Imagine a doughnut shaped superconductor, when an electrical current is applied, it will have this current traveling around its circular cross-section. These “supercurrents” pay homage to their name in that, according to Y.B. Kim and colleagues, the fastest magnetic field decay rate found in certain specimens has been 10 gauss per decade, a gauss being a scientific measure of the strength of the magnetic field induced by the persistent current, and are estimated to subside completely in $3 \times 10^{19}$ years, or nearly an eternity! Typical conductors such as copper, gold, and platinum do not experience this persistency as superconductors do.

![Figure 1: Resistance of a specimen of mercury versus absolute temperature (K). This plot by Kamerlingh Onnes marked the discovery of superconductivity.](image-url)
2. They undergo the Meissner Effect in the presence of a magnet. Before delving into what the Meissner Effect is, it is important to understand the concept of transition temperatures. Transition temperatures, or critical temperatures ($T_C$) as I will be calling them in the context of this study, are the specific temperatures at which a material experiences superconductivity. When a typical magnet of sufficient strength is cooled below the $T_C$ of a superconductor, this superconductor will levitate atop the magnet at a fixed distance. This effect is known as the Meissner Effect, and it is the backbone concept behind novel magnetic levitation rail system designs.

“Kamerlingh Onnes observed the first superconducting state of a material when he cooled mercury below a temperature of 4.2K and found that the resistance suddenly dropped to less than $10^{-6}$ Ω (ohms),” nearly zero (van Delft and Kes 2010). For years to come, other metals were found to have superconducting characteristics. In the 1960’s "certain alloys of niobium were made that became superconductors at 10-23K. It was generally believed on theoretical grounds that there would be no superconductors above 30K" (Sheahen). However, everything soon changed in 1986 with the birth of what is now known as high temperature superconductivity (HTS).

The infant field of high temperature superconductivity (HTS), aside from ordinary superconductivity, began to take shape when “in late 1986 news spread that J. George Bednorz and Karl Müller of the IBM research laboratory in Zurich, Switzerland, reported the superconductivity in lanthanum copper oxides doped with barium or strontium at temperatures up to 38K” (Sheahen). Soon after, many scientists began to stake their claim in superconductivity, all rushing to find a material with an even greater $T_C$. Once a $T_C$ of 77K was reached, high temperature superconductivity was born.

One might ask what the importance of a 77K $T_C$ might be. How is that a significant number and why does it come into play with HTS? The answer itself is a question of how low can you go. Liquid helium which can cool materials to about 4K (at a high cost of nearly $7 per liter) which is much more expensive compared to liquid nitrogen, which cools at 77K, and can be obtained by the truckload at a mere 6¢ per liter. This colossal price difference marks the disparity between the superconductors that require helium, LTS, to those only needing nitrogen, HTS. Known physical laws prevent a superconductor functioning at room temperature, and so,
many researchers have detoured in finding the highest $T_C$ possible in exchange for researching and developing the capacities and characteristics of known materials.

Unfortunately, HTS are not perfect. Like most ceramics, HTS are very brittle, preventing their immediate use as wires for telecommunication or power lines. Equally limiting is the fact that they do not carry sufficient current to be used in the real world just yet. This leads us to bismuth strontium calcium copper oxide (Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{11-\delta}$) or BSCCO for short.

The crystalline, or atomic unit cell, of BSCCO is anisotropic (its properties are quite different and complex in various directions) and consequently shears off easily along a certain plane, thus allowing for it to be shaped and deformed with less difficulty than other ceramic HTS. This material can be wound up for wire applications, for example. Although having this advantageous characteristic, the complexity within the structure of these “new school” superconductors limits the strength of magnetic flux pinning. Flux pinning is the phenomenon where the magnetic field lines become trapped or "pinned" inside a superconducting material. This “pinning binds the superconductor to the magnet at a fixed distance and is only possible when there are defects in the crystalline structure such as impurities” which are purposely added to the material, much in the way salt is incorporated in many recipes to amplify the flavor of other ingredients (Eck 2007). “Nonmagnetic impurities [such as lead] have no very marked effect on the transition temperature” of superconductors (Kittel 2004). Flux pinning is desirable in high-temperature ceramic superconductors in order to prevent "flux-creep" (flux escape), which can create a pseudo-resistance, hence reducing the critical current density ($J_C$) and critical magnetic field ($B_C$), reducing the efficiency and capacity of the superconductor.

In the case of HTS, they only exhibit a partial expulsion of an incoming magnetic field from its borders, consequently having two critical magnetic fields: $B_{C1}$ and $B_{C2}$. When an HTS is in the presence of a magnetic field in the range between the two critical magnetic fields ($B_{C1}<B<B_{C2}$) the material is said to be in the vortex state, in that it experiences optimal superconducting electrical properties. It is within the vortex state that university and industrial investigators are enthusiastically searching for different ways of exploiting the electromagnetic properties of HTS.

![M3D model of BSCCO-2212](image1)

![The complex unit structure of BSCCO.](image2)

![Magnetization versus applied magnetic field with the critical magnetic fields for both LTS and HTS.](image3)
With respect to BSCCO, it has been found after multiple tests with varying proportions, that doping it with a specific amount of lead (Pb) will not alter the structure of the material, but theoretically increases the critical current density ($J_C$). Our investigations will adequately map the impact of Pb doping on critical current density as well as other essential properties.

**Procedure of Sample Preparation**

The bulk superconducting material $\text{Bi}(2)\text{Sr}(2)\text{Ca}(2)\text{Cu}(3)\text{O}(11-\delta)$ is a polycrystalline structure made by solid-state reaction method. Two samples of doping ratios 0.1, 0.3, 0.4, and 0.5 were made by the nonstochiometric mixture of bismuth oxide ($\text{Bi}_2\text{O}_3$), lead oxide (PbO), strontium carbonate ($\text{SrCO}_3$), calcium carbonate ($\text{CaCO}_3$), and copper oxide (CuO), resulting in 10g of product. Nonstochiometric mixtures are combinations in which the atomic composition cannot “be expressed as a ratio of small whole numbers” (McMurry and Fay). Varying the Pb doping levels, the empirical formula for BSCCO is now represented by:

$$[\text{Bi}_{2-x}\text{Pb}_x]_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{11-\delta}$$

where “$x$” denotes the ratio amount of Pb doping and “$\delta$” is a varying ratio amount of oxygen that does not affect the superconducting properties of the material appreciably.

Each sample mixtures were placed in small ceramic crucibles into a Thermolyne 48000 series furnace, heated up to 850°C (1123K) at a rate of 35°C/hr. This temperature is maintained for 100 hours before cooling down to room temperature at 60°C/hr. After grinding the product down to a fine powder, the above procedure is repeated a second time for proper composition.

**Theoretical Results/Discussion**

Considering the length of time required for the baking procedure of each sample, concrete results for this study are yet to be presented, but the “critical current density studies will include devices, made available to us by a collaborator in Japan” (Zhang). To begin, a direct electrical current will be applied from a power supply to the superconductor. A predetermined amount of current is applied, one that the undoped BSCCO material is known to contain, then slowly increased until the superconducting state is exterminated; this will give the set amount of $J_C$, which the doped material can hold.

The hypothesis emerging from extensive literature review is that the ideal doping ratio of lead within BSCCO should be between 0.3 and 0.4. This undefined ratio amount will attribute “high magnetic flux pinning within the material, as well as a higher load of critical current density, $J_C$” (Zhang, Liu, et al. 1991). The sample that meets these criteria will contain the ideal Pb doping, within the limits of our study, opening wider the door for the development and application of a high temperature superconductor such as BSCCO for feasible real-life purposes. Possible fields of application include telecommunications and magnetic resonance imaging.
Bibliography


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