Thin Film Oxides: The Superconductive YBCO and Non-Superconductive ITO

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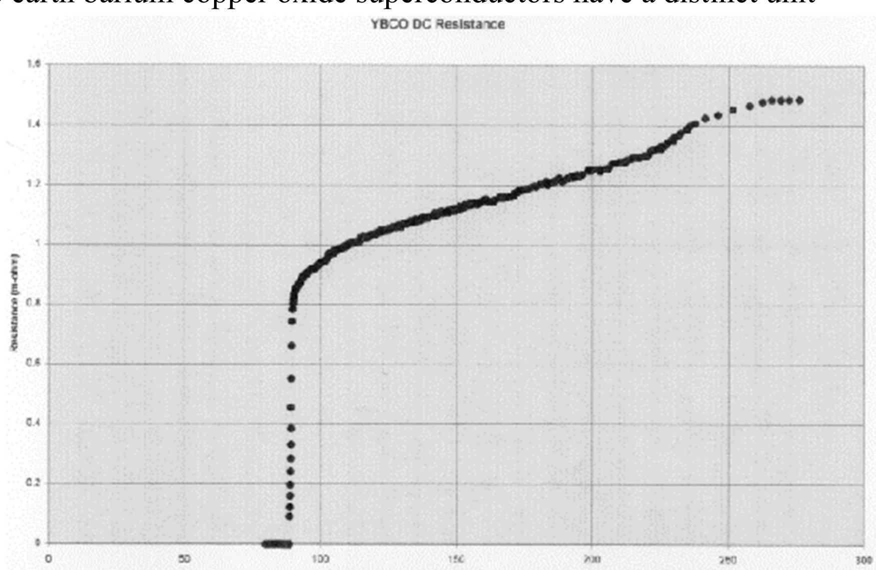
Introduction

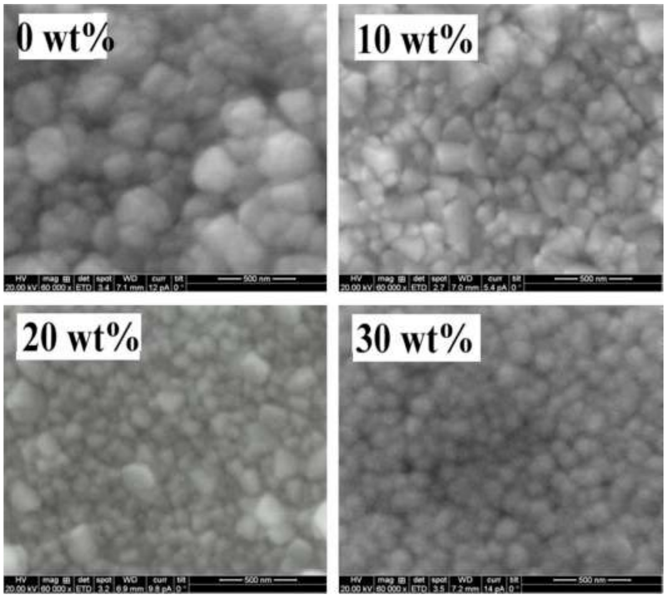
Yttrium Barium Copper Oxide (YBCO) is the first high-temperature cuprate superconductor to ever be discovered, and to this day remains a leading compound in the list of unconventional superconductors not explained by BCS theory. In stark contrast lies Indium Tin Oxide, another conducting oxide that can't demonstrate the Meissner effect. Both YBCO and ITO are primarily grown in thin films, and both function as conductors in less extreme conditions, but something that differentiates ITO from YBCO causes the former to be unable to attain superconductivity. The intent of this paper is to identify what exactly this feature may be.

Characterizing YBCO and ITO

The superconductivity of YBCO is a well-established and broadly accepted scientific fact at this time. YBCO and other rare earth barium copper oxide superconductors have a distinct unit cell consisting of a central rare earth atom (Yttrium, in this case) bounded by conducting Cu-O planes which themselves form a cubic lattice surrounding barium atoms. YBCO has a critical temperature of approximately 93K at atmospheric pressure, as can be seen in the figure to the right.



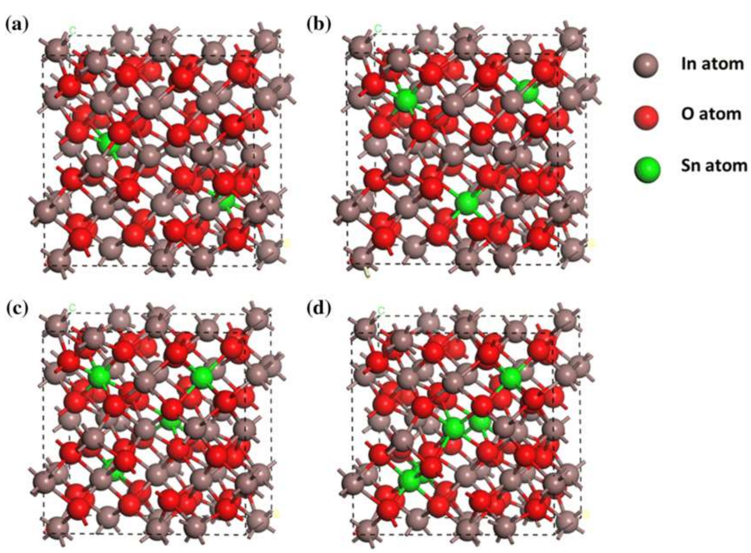
In this figure, the Meissner Effect can be seen as the resistance of YBCO falls to 0 below the critical temperature, signifying the phase transition from normal conductor to superconductor. As I will discuss later, superconducting YBCO thin films have a host of other properties that distinguish them from compounds like ITO. Before that, however, ITO itself must be characterized.

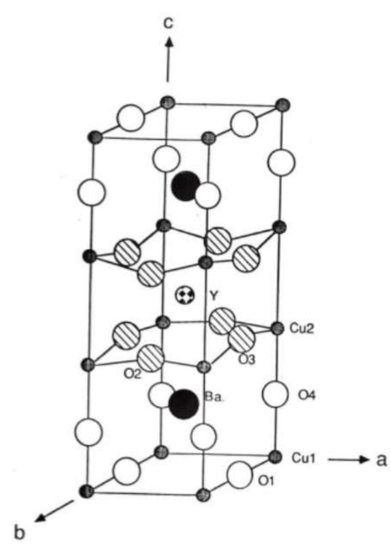


ITO is a semiconductor composed of Tin-doped indium oxide groups that form in cubic polycrystalline thin films, with preferential growth in the (222) or (400) planes of the corresponding Miller indices. In general, the percentage of tin present in the lattice has many effects on the resulting compound, as seen to the left. In this figure, it is easy to see that as Sn concentration increases, the particulate grains of ITO grow finer and more dense, contributing to its ever-increasing conductivity and optical transmittance. ITO also gets increasingly hydrophilic as the tin saturation increases, which directly corresponds to the increasing free charge contributed by the tin in the compound. This same free charge is what makes ITO an ideal conductor, which, along with its low absorption spectrum with high tin content, makes it an ideal transparent conducting oxide.

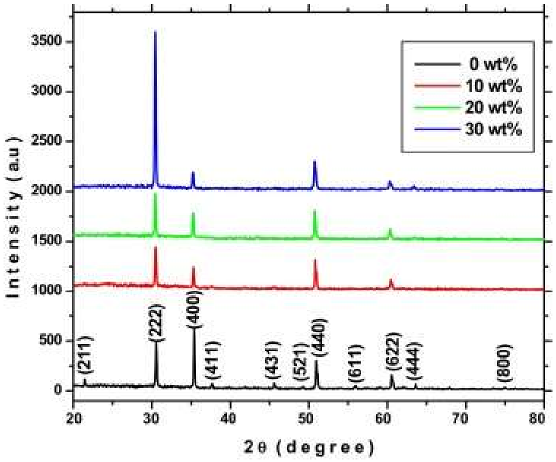
Lattice Structure

To more deeply analyze ITO and YBCO, let us first contrast the most clear and easily evident source of difference between the two: Their lattice structures. Depicted below are the lattice structures for ITO of varying Sn concentrations (left) and YBCO (right).





To help further distinguish the two, below are the diffraction patterns of ITO of varying tin concentrations (left) and YBCO (right).



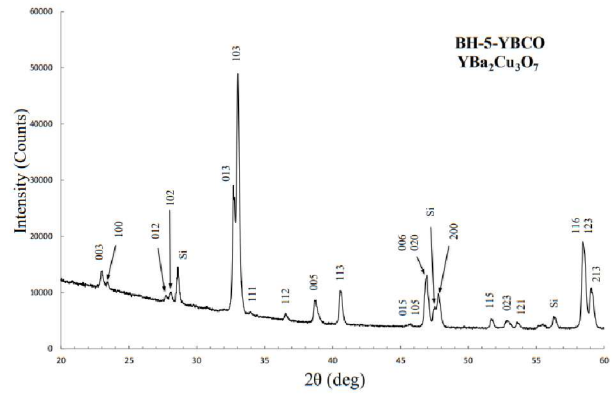


Figure 6: X-ray Diffraction pattern with indexed peaks of sample BH-5-YBCO with composition $YBa_2Cu_3O_7$. Silicon standard peaks are also labeled.

Just like with ITO and tin content, YBCO can have varying degrees of oxygenation, which results in minor differences in lattice structure. In the case of YBCO, the lattice is extremely orderly, consisting of a central Yttrium atom bounded on either side by a conducting O3 Cu2 square plane. On both the top and bottom-most thirds of the primitive lattice, there is something resembling a body-centered cubic lattice characterized by a pair of conductive O1 Cu1 chains running opposite the conducting square plane.

These conducting planes and chains of oxygen are crucial to the superconductive properties of YBCO: In a sample of oxygen content 6.33 (fully saturated YBCO has an oxygen content of 7), the critical temperature T_c came down to an astounding 10K from the fully saturated T_c of ~93K. Although the lattice structure didn't change much with decreasing oxygen content, oxygen and copper together provided ways for current to flow through a YBCO lattice in geometrically predictable and orderly ways. Although it's not obvious why this so strongly correlates with the superconductivity of YBCO, it at the very least plays a big role.

In contrast to the orthorhombic YBCO, ITO has a cubic primitive lattice. Rather than having any simple conductive planes or chains, instead, ITO is an n-type semiconductor, with high energy Sn-electrons just under the conduction band that can be excited into a conducting state through the simple application of an external electric field. It does not rely on conductive planes or chains, instead entirely gaining conductive status from the free electrons coming from the embedded Sn atoms.

This is why Sn concentration so strongly correlates with conductivity in ITO, while in YBCO, oxygen correlates with conductivity instead. ITO relies on tin doping to achieve semiconductive status while YBCO relies on discrete paths of current to achieve a Meissner state. This comes as a result of both the Sn doping of ITO as well as the relative complexity of its unit cell as compared to YBCO.

Electrical Conductivity

The conductivity of ITO and YBCO at room temperature vary by a factor of between 2 and 4, which is to be expected based on what has already been seen of their lattice structures. However, the conductivity alone cannot present a wholistic view of the properties of either YBCO or ITO, since both can vary significantly in oxygen content for the former and Sn content for the latter.

Attached below is the set of conductivities for YBCO of samples of varying oxygen concentrations, resulting in varying phase boundaries. Here, they've been characterized by their critical currents at 30K, while the conductivity measurements are given as recorded at room temperature.

Ic= CriticaL Current(mA)	Jc=CURRENT DENSITY (A/m2)	ρ=Resistivity (Ωm)	σ= Conductivity
7	0.2147687×10^{3}	--	--
19	0.5829436×10^{3}	--	--
32	0.9817998×10^{3}	--	--
45	1.3806560×10^{3}	$0.10212536 \times 10^{-3}$	9.791887×10^{3}
50	1.5340623×10^{3}	0.0369851×10^{-3}	27.03915×10^{3}
70	2.1476872×10^{3}	0.0330284×10^{-3}	30.28624×10^{3}
80	2.4544997×10^{3}	0.0346736×10^{-3}	28.84038×10^{3}

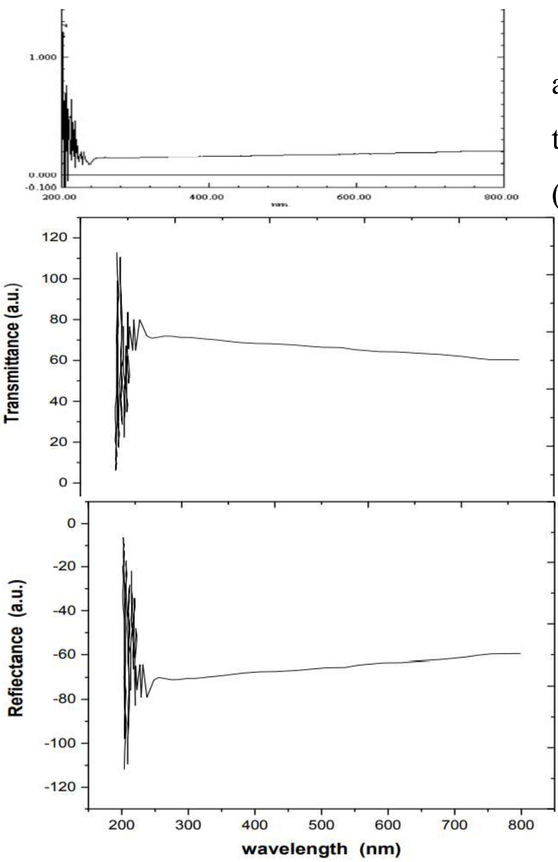
In contrast, ITO with 5.7% wt Sn has a conductivity of around $1.3 * 10^4$.

The oxygen content of these YBCO samples was not measured, but the nearest value of YBCO conductivity as recorded here occurs with the I_c = 45 mA sample, which both can be rounded to approximately $1 * 10^4$. YBCO of higher oxygen saturation has nearly triple the conductivity of this ITO sample.

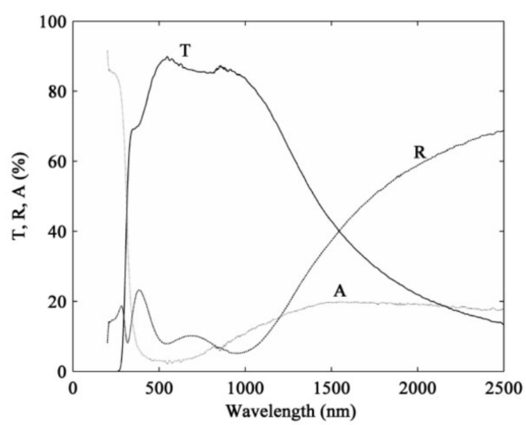
It is interesting to me that the conductivities of 45 mA I_c YBCO and 5.7% wt Sn ITO are so similar, considering how differently each of their lattices behave in a normally conductive state. The conductivity of YBCO arises from chains and planes of copper and oxygen atoms that allow electrons to freely flow in parallel about the central yttrium atom, forming an orthorhombic structure with highly regular patterns of electron movement. In contrast, conductive ITO, which relies on the high energy valence electrons of Sn atoms to turn it into a conductor under external electric fields, does not have such clean and straightforward pathways on which charge can flow. Both of their conductivities being so similar under normal conditions and atmospheric pressure, then, becomes quite fascinating.

At present, it does not seem as though the mechanics behind each of their conductivity gives them an edge in typical conditions, but that the regular structure of rare earth copper oxides instead only gives them an edge when transitioning into a Meissner state.

Optical Properties



To the left are the absorption (top), transmittance (middle), and reflectance (bottom) spectra of pure YBCO at room temperature to the left. Below, we have a graph of the transmission (T), reflection (R), and absorption (A) of ITO at 673K.



In either case, the reflection spectrum is indicative of a larger feature: The amplitude of reflectance and the carrier concentration of each sample are strongly linked, yet the results differ quite dramatically. In the case of YBCO, reflectance is positively correlated with oxygen content, while in ITO, it is negatively correlated with oxygen content. This indicates that while the Cu-O groups of YBCO are core to its conductivity, the oxygen atoms in ITO instead increase resistance and correlate to a decrease in carrier density.

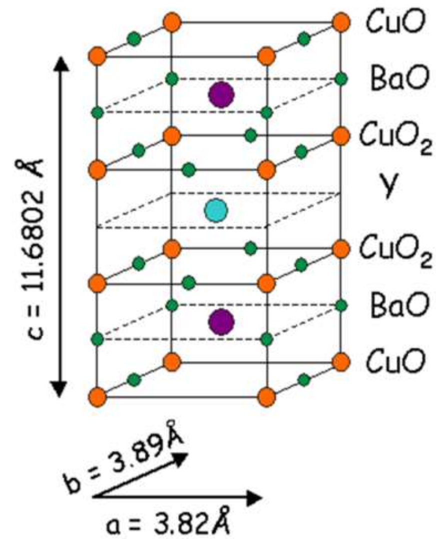
Though the temperatures of these spectra differ significantly for YBCO and ITO, the underlying physics is still exposed: Fundamental to the difference in their behavior as conductors is the fact that their lattice structures conduct electricity in two entirely different ways.

For YBCO itself, these measurements yield an optical energy gap of 5.02 eV, which is reduced as oxygen levels increase due to the increased absorption of incoming low-energy photons. Considering that oxygen content in YBCO also correlates with both a higher T_c and a higher carrier concentration, we can begin to examine YBCO itself.

The Status of YBCO

Generally speaking, YBCO is thought to be unconventional due to the fact that its mechanisms of conducting plains and chains of copper and oxygen don't suit the attractive potentials thought to be behind the formation of cooper pairs, necessary for the formation of the Bose-Einstein condensate considered by some to be responsible for superconductivity.

Between all rare earth barium copper oxide superconductors, the copper oxide planes and chains are the common link, implying that they are responsible for the superconductivity of these systems, with the central rare earth metal being primarily needed for structural integrity of the lattice. Notably, it is demonstrable that the barium and yttrium layers aren't conductive by themselves, bearing no free electrons or paths for those electrons to move. However, owing to the fact that copper oxide planes by themselves cannot achieve superconductivity, it can be concluded that these planes are vital to the Meissner state of YBCO.



There are certain theories that the spin interaction between cooper pairs and planar ions is what explains the superconductivity of YBCO and similar cuprate superconductors, but the simple fact remains that unless modified, BCS theory cannot explain the mechanism for YBCO's superconductivity, especially due to its mixed partially superconductive state, characterized by vortex pinning across irregularities in the lattice. As a result, the general consensus of YBCO as an unconventional superconductor holds much weight, and thus highlights a glaring shortcoming in BCS theory as it exists today.

Conclusion

Comparing the lattice structures alongside the electric and optical properties of YBCO and ITO sheds light on differences in how these two conducting oxides function.

ITO requires Sn atoms within the lattice to provide valence electrons that can be elevated to the conduction band with the help of a small external electric field, at which point the electrons become free to move as in a typical conductor. Oxygen serves as an insulator in ITO, and the reflection profile indicates that it decreases the carriers present.

In stark contrast, YBCO has regular conductive CuO_2 planes, as well as bidirectional conducting CuO chains. These are always able to conduct electrons, and limiting oxygen reduces the carriers present in the YBCO lattice, thus increasing its resistivity and lowering the critical current and temperature of the compound's Meissner state.

Despite being conducting oxide thin films, YBCO and ITO could not be further from one another in terms of their mechanism of conduction, which may hold insight for why YBCO can demonstrate the Meissner effect while ITO cannot. On its own, YBCO's mechanisms for superconductivity are not strictly consistent with BCS theory, and its partial superconductor state confirms its status as an unconventional superconductor.

References:

ITO Sources

ITO High-Temp Optical properties

https://www.nature.com/articles/s41598-020-69463-4

ITO Lattice Structure, Optical/Electrical Properties, Pyrolysis

https://www.sciencedirect.com/science/article/pii/S2187076415300452#:~:text=Indium%20tin%20oxide%20(ITO)%20is,bind%20with%20the%20interstitial%20oxygen.

High temp. conductive stability of ITO

https://www.frontiersin.org/articles/10.3389/fmats.2020.00113/full

General ITO properties

https://www.msesupplies.com/pages/material-properties-of-indium-tin-oxide-ito

ITO Thin Film Optical/Electrical Properties, DC Magnetron Sputtering

https://arxiv.org/ftp/arxiv/papers/1409/1409.5293.pdf

YBCO Sources

Crystal structure and Superconductivity of YBCO
https://cornerstone.lib.mnsu.edu/cgi/viewcontent.cgi?article=1345&context=etds

Synthesis, Optical, and Electrical Properties of YBCO at Room Temp
https://www.iosrjournals.org/iosr-jap/papers/Vol13-issue2/Series-2/F1302023948.pdf

Simple YBCO measurements nearing phase transition
https://phys420.phas.ubc.ca/p420_96/bruce/ybco.html

Electrical Properties of Superconducting YBCO
https://www.ncbi.nlm.nih.gov/pmc/articles/PMC8235488/

New research on YBCO Flux Pinning
https://physics.aps.org/articles/v10/129

Synthesis and Characterization of YBCO
https://core.ac.uk/download/pdf/80148202.pdf