

Synthesis and Characterization of
 $\text{LaBa}_2\text{Cu}_3\text{O}_7$ and $\text{PrBa}_2\text{Cu}_3\text{O}_7$

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Abstract

Both $\text{LaBa}_2\text{Cu}_3\text{O}_7$ and $\text{PrBa}_2\text{Cu}_3\text{O}_7$ were synthesized using a method that has been used to produce high quality (onset $T_c=101$ K) $\text{LaBa}_2\text{Cu}_3\text{O}_7$. The method attempts to prevent Lanthanide substitution on the Ba site by depleting the material of O_2 at high temperatures. This first attempt failed. The $\text{PrBa}_2\text{Cu}_3\text{O}_7$ did not bulk superconduct and the $\text{LaBa}_2\text{Cu}_3\text{O}_7$ had an onset $T_c=60$ K.

Background

In the early 1900's many scientists were exploring the affect of low temperatures on electrical resistance in conductors. Heike Kamerlingh Onnes made a major contribution to this field in 1908 when he discovered a process to liquefy helium. This process lead Onnes to the discovery of superconductivity in solid mercury at 4.19 K in 1911. Superconductivity research has continued ever since.

Superconductivity is characterized by a material having no electrical resistance and exhibiting perfect diamagnetism, the Meissner Effect. The temperature at which a material becomes superconducting is its critical temperature (T_c). In 1957 a theory that successfully explained superconductivity was developed and accepted. The theory was purposed by Bardeen, Cooper, and Schrieffer, and is known as the BCS theory. This theory is based on the formation of electron pairs, called Cooper pairs, in the superconducting state. The electrons are attracted by vibrations in the lattice structure, known as phonons. These attractive phonon interactions overcome the repulsive Coulomb interactions between the electrons. The attractive phonon interaction can be thought of as a wake of positive charge density that follows an electron. As an electron travels through a lattice, its negative charge pulls the positively charged nuclei of the lattice toward its path of travel. Another electron then is attracted to the increased positive charge density that follows an electron and the attraction forms a Cooper pair of two electrons with opposite momentum and spin. The

formation of Cooper pairs causes an energy gap, which makes it impossible for electrons to lose small amounts of energy. It is this affect of Cooper pairs that causes superconductivity.¹

In 1986 Bednorz and Mueller discovered the first “high temperature” superconductor. It was a lanthanum-based cuprate perovskite with a T_c of 35 K. Shortly after this discovery, it was found that a similar yttrium-based material,

$\text{YBa}_2\text{Cu}_3\text{O}_7$ (Y123), shown in Figure 1, had a T_c of 92 K. This was an important break through because the T_c was greater than the boiling point of liquid nitrogen (77 K), which meant that the superconducting material could be cooled much more inexpensively. The new high-temperature superconductors (HTSC) also brought

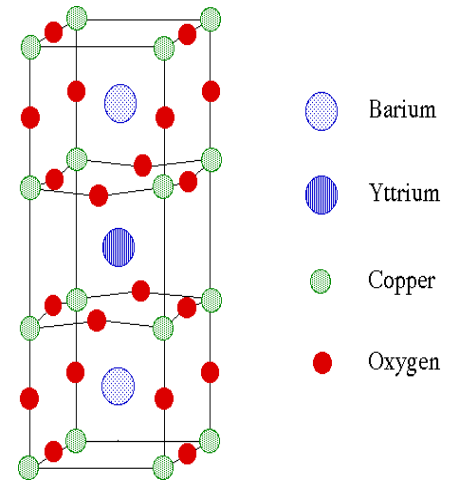


Figure 1: $\text{YBa}_2\text{Cu}_3\text{O}_7$

about the need for a new superconductivity theory. The

BCS theory’s mechanism for creating Cooper pairs no longer worked at the new high T_c .

There is still no widely accepted theory that successfully explains the phenomena of HTSC.

Introduction

One well known theory for the explanation of HTSC relies on the existence of electron pairs within the copper planes of HTSC. Throughout this paper this theory will be referred to as the copper-plane theory. There is considerable evidence to cause one to doubt this theory. Much of this evidence can be discussed within the context of a comparison between $\text{LaBa}_2\text{Cu}_3\text{O}_7$ (La123) and $\text{PrBa}_2\text{Cu}_3\text{O}_7$ (Pr123). Both of these materials have homologous structures yet the La123 regularly exhibits bulk superconductivity with a T_c around 98 K and Pr123 typically does not exhibit bulk superconductivity. The copper-plane theory offers a couple explanations as to why the Pr123 does not superconduct. One explanation, the charge-fluctuation explanation, is that the Pr is ionized to Pr^{+4} , which would differentiate it from the La^{+3} counterpart. The extra lost electron from Pr^{+4} is accounted to fill a hole that is

necessary for the formation of Cooper pairs in the copper plane theory. A second explanation, the spin-fluctuation explanation, suggests that the Pr breaks Cooper pairs in the copper planes because it is magnetic, while La does not break the Cooper pairs because it is not magnetic.² Both of these explanations seem plausible, but neither correspond to experimental evidence. For example, the copper-plane theory would suggest that Pr123 cannot superconduct under any circumstances. However, Pr123 does show inhomogeneous superconductivity, which was observed both by resistance and magnetization measurements.^{3,4}

The charge-fluctuation explanation, if valid, should imply that any similar +4 ion within material isostructural to the Y123 class should stop, or at least impede superconductivity. This is not the case for Y123 doped in the Y spot ($Y_{1-x}Tb_xBa_2Cu_3O_7$) with Tb, which is known to ionize to Tb^{+4} . The Tb doping does not stop or impede the superconductivity.² Also, there are other isostructural materials with +3 ions that do not superconduct. For example $CmBa_2Cu_3O_7$ does not superconduct, yet isostructural $GdBa_2Cu_3O_7$ does superconduct. Both Cm and Gd form +3 ions and have very similar electron configurations. These two examples show that the difference in ionization from +4 to +3, is not directly related to the superconductivity of the Y123 class of superconductors. The spin fluctuation explanation has similar inconsistencies. As mentioned above, $GdBa_2Cu_3O_7$ superconducts, yet Gd is very magnetic, more magnetic the Pr actually. This strongly suggests that Pr123's tendency to not bulk superconduct is not directly caused by the magnetic moment of Pr.

While the copper-plane theory fails to explain why Pr123 does not typically bulk superconduct, a more successful explanation does exist. This explanation relies on the superconductivity existing within the copper chains of the lattice rather than the copper planes, and therefore will be referred to as the copper-chain explanation. This theory shows that it is a combination of Pr's magnetic moment and its ionic size that makes Pr123 not superconduct. Pr^{+3} is large enough to substitute into the Ba^{+2} site without greatly distorting

the lattice. A plethora of data supports the existence of Pr^{+3} on the Ba site in Pr123.² Other large lanthanide ions, such as La^{+3} , Ce^{+3} , and Nd^{+3} can also occupy the Ba site, but simply being able to occupy the Ba site does not destroy superconductivity. Recall La123 is a great superconductor. To stop superconductivity an ion must be both magnetic and able to occupy

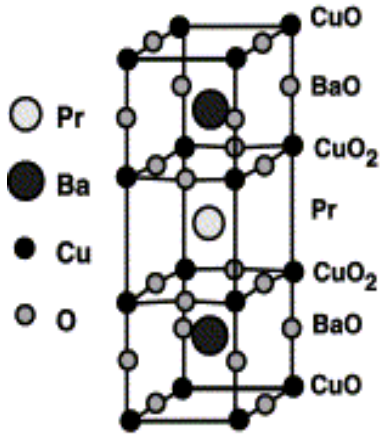


Figure 2: $\text{PrBa}_2\text{Cu}_3\text{O}_7$

the Ba site. The presence of a magnetic ion near the copper-chains, shown in Figure 2 for Pr123 with the copper chains labeled CuO and the planes labeled CuO₂, is responsible for stopping superconductivity. The copper chains are close enough to the Ba site for magnetic ions in the Ba site to affect electrons within Cooper pairs. The magnetic field causes the two electron spins to align, which breaks the Cooper pair and stop superconductivity. This is why Pr123 does not bulk superconduct. Gd123 does however superconduct because Gd, while it is magnetic, is too small to appreciably substitute into the Ba site. From its proper position, often called the rare earth site, its magnetic field is too weak to affect the Cooper pairs in the copper chains (recall magnetic field is proportional to r^{-3}). So in summary Pr123 does not superconduct because Pr^{+3} is magnetic and is susceptible to occupy the Ba site.

Considering the aforementioned explanation, it is logical to assume that Pr123 could bulk superconduct if there were a method to prevent Pr from occupying the Ba site. The previously observed inhomogeneous superconductivity in Pr123 also supports this assumption.^{3,4} It has been observed, and is consistent with chemistry, that Pr substitution on

the Ba site is accompanied by an extra O in the copper chain layer as is shown in Figure 3. The same process is involved for La in the Ba site. La in the Ba site does not stop superconductivity, but it does lower the T_c of the La123. High T_c La123 (101 K onset and 97 K $R=0$) has been created by a synthesis process which involves sintering La123 material in an oxygen depleted environment to prevent La

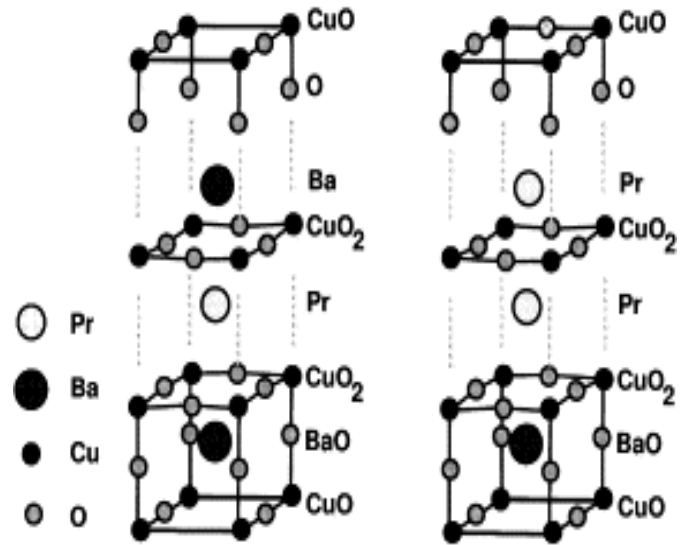


Figure 3: Structural difference between superconducting (left) and non-superconducting (right) $\text{PrBa}_2\text{Cu}_3\text{O}_7$

substitution in the Ba site.⁵ In this experiment La123 and Pr123 were both synthesized following this same method in an attempt to create bulk superconducting Pr123.

Synthesis

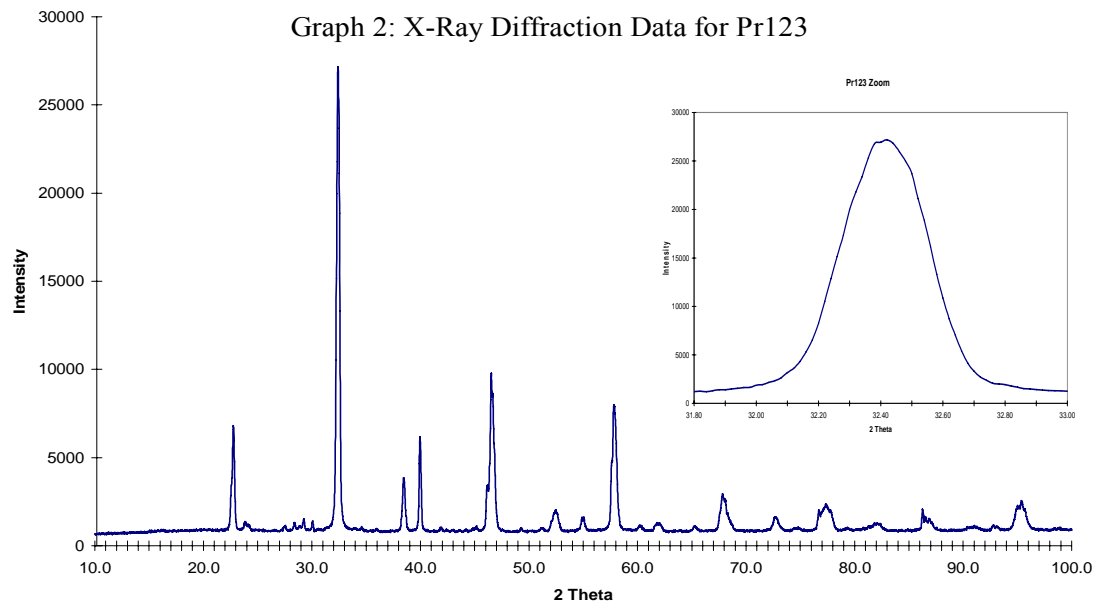
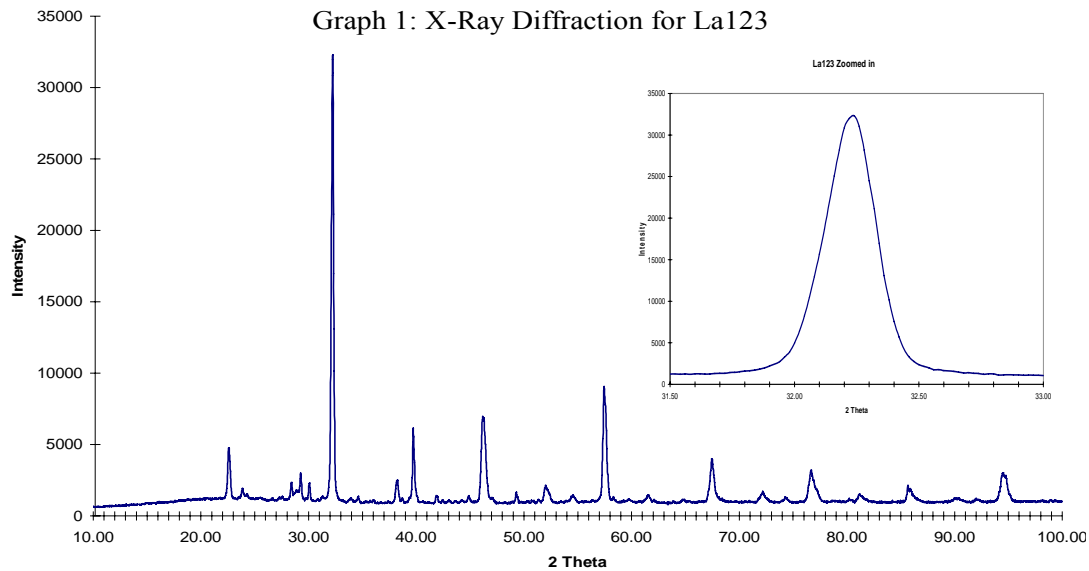
The starting materials used to create La123 and Pr123 were La_2O_3 and Pr_6O_{11} respectively, each with BaCO_3 and CuO . Each starting material was at least 99.99% pure and had previously been heated to eliminate any water impurities due to the materials hygroscopic nature. Starting materials were weighed out in proper stoichiometric ratios to produce 10 g of powder for both La123 and Pr123. Both the powders were mixed by hand grinding with mortar and pestle for 1 hour. The Pr123 was then heated at 825 °C for 17.25 hours in air approximately following the procedure in [5]. Due to an error, the La123 was treated with a different heat treatment. It was heated at 900 °C for 20 hours after a 3.5 hour ramp up from room temperature. The 20 hour phase and an 18 hour ramp down to room

temperature were both done in a flowing N_2 gas environment. Aside from this difference, both materials received the exact same treatment, and were even heated simultaneously in the same furnace. The initial heating step is primarily intended to remove the C from the $BaCO_3$ and is called calcinations. Following the initial heat treatment both materials were hand grinded by mortar and pestle for an hour, then each pressed into 3, 1.00 g pellets under 10,000 psi of force. This is done to densify the materials, which will make them more intimately mixed and more likely to react. All the pellets were placed in an aluminum oxide dish in 2 stacks separated by material. They were both heated for 20 hours at $900\text{ }^\circ\text{C}$ following a 3.5 hour ramp up from room temperature. They were in a flowing N_2 gas environment after the initial ramp and remained in that environment until the conclusion of an 8.75 hour ramp down to room temperature. This step is called sintering and is when the product should have formed, which is why O_2 was depleted from the environment to prevent Ba site substitution. Following this step, room temperature resistance measurements were made on the pellets in order to qualitatively check their progress. The Pr123 resistance was lower than it had been on past attempts, and the La123 resistance was low as was expected. The pellets were heated once more at $400\text{ }^\circ\text{C}$ for 55 hours after an 8 hour ramp up and followed by a 26.33 hour ramp down to room temperature. This heating step, annealing, was done in an environment of flowing O_2 to replace any oxygen that was lacking while sintering. The temperature for this process is too low for Ba site substitution so the presence of O_2 should not have a negative affect. Following this step, the electrical resistance of both materials was once again tested, and was even lower than the previous test. This was thought to be an indication of well formed materials.

Characterization

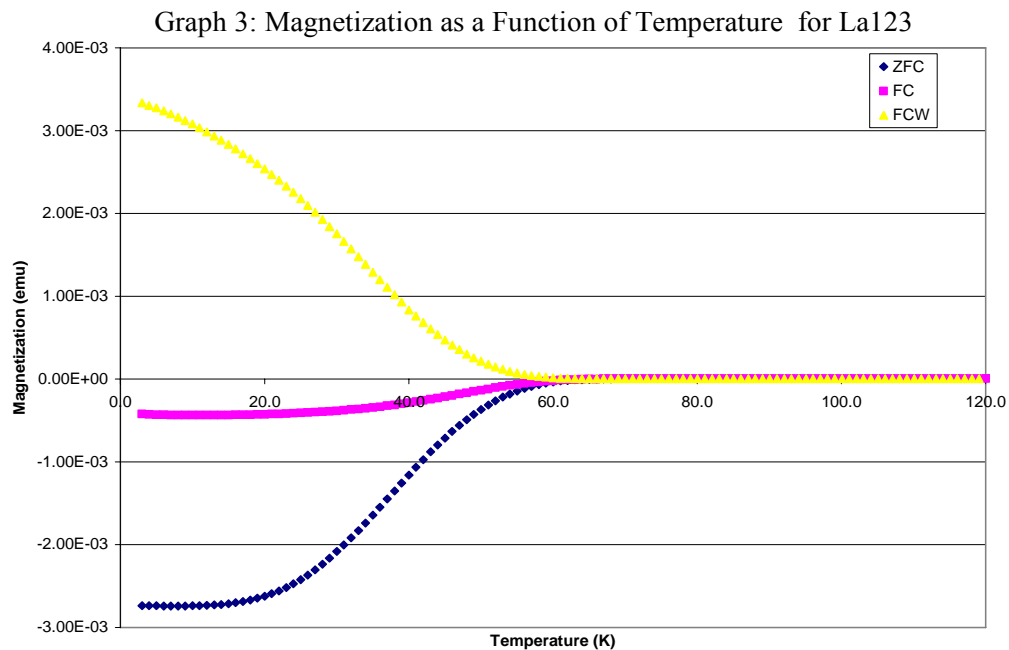
Both materials were characterized using powder x-ray diffraction and SQUID measurements. These techniques were used to primarily provide qualitative feedback on the material. The x-ray data gives some useful information on the structure of the desired products, and the SQUID data shows the products magnetic properties, which indicates whether or not the materials superconduct and at what T_c .

Half of the top pellet of each material was ground up with a mortar and pestle to provide powder samples to be used for x-ray diffraction. The x-rays were taken from 10 - 100° (shown as 2θ , where θ is the traditional angle used in Bragg's Law) at a rate of $0.12^\circ/\text{min}$. A key feature seen in well formed Y123 class superconductors is the splitting of major peaks which is caused by an orthorhombic lattice, meaning all three of the lattice constants are not equal. This feature was not seen in either of the material's x-ray data, which indicates a lack of oxygen in the copper chains, causing the a and b lattice constants to be equal. Longer annealing periods could possibly provide the needed oxygen. Also, each material's diffraction pattern was compared with the pattern of the starting materials. Several BaCO_3 peaks matched which suggests the presence of un-reacted BaCO_3 in the samples. This observation would also suggest that there may be Pr and La filling the Ba sites, which would otherwise be filled with the Ba from the un-reacted BaCO_3 . The substitution could have possibly occurred in the high-temperature portion of the sintering heat ramp up, because the flowing N_2 gas was not applied until the ramp was complete. Figures 1 and 2 show the x-ray diffraction patterns from La123 and Pr123 respectively, and show the largest peak blown up to demonstrate the lack of split peaks. In summary, the x-ray diffraction suggests that the materials did not fully form, which coincided with them not having great superconductivity.



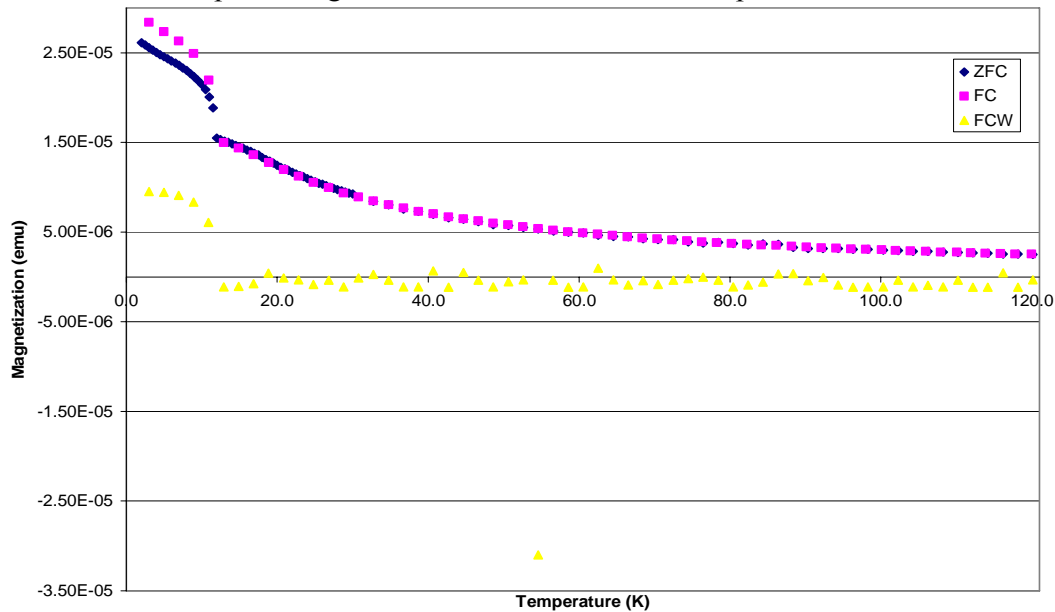
The SQUID (superconducting quantum interference) data confirms this analysis. The SQUID is essentially a very sensitive magnetometer that was used to produce graphs of magnetization as a function of temperature. Each graph shown records 3 sweeps of a temperature range. The first sweep is the zero-field cooled (ZFC) sweep which measures the samples magnetization in an applied magnetic field while heating after the sample had been cooled to 2 K in the absence of a field. The second sweep measures the magnetization in an applied field while cooling the temperature and is called field-cooled (FC). The third sweep is called field-cooled warming and measures the magnetization in the absence of a field while increasing the temperature.

Graph 3 shows the SQUID data for La123. The presence of diamagnetism, seen by negative magnetization in an applied field, shows that the La123 does superconduct (recall the Meissner Effect). The onset of the superconductivity occurs where the diamagnetism begins around 60 K, which is a poor T_c for La123. The magnetization slowly decreases rather than sharply decrease which is another sign of poorly formed La123. The positive field cooled sweep is from flux trapping within the material. This is typical of La123. Overall the SQUID data shows that the La123 did not fully form, and is also likely to contain La on the Ba site. The deviation from the procedure used in [5] in the initial heating process could be one cause of the poorly formed material



The SQUID data for Pr123 was noisier than for the La123, but also indicated poor product formation. The Pr123 did not show significant diamagnetism (the one significantly diamagnetic point is considered noise) which indicates that it was not superconducting. This is likely to be caused by magnetic Pr^{+3} ions occupying Ba sites.

Graph 4: Magnetization as a Function of Temperature for Pr123



Conclusion

An attempt was made to synthesize superconducting $\text{LaBa}_2\text{Cu}_3\text{O}_7$ and $\text{PrBa}_2\text{Cu}_3\text{O}_7$ by using a process designed to prevent Ba site substitution by depleting the materials of oxygen during the sintering step. The SQUID and x-ray data both indicate that the process failed to produce high quality La123 and bulk superconducting Pr123. The failure is likely due to incomplete product formation and Ba site substitution. The process will be altered to involve less O_2 exposure at high temperatures, and longer annealing periods to replenish depleted oxygen at low temperatures.

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