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To cite this article: Emetere M.E. *et al* 2020 *J. Phys.: Conf. Ser.* **1622** 012068

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Evidence of Polarons and Bipolarons in a Chemically Pressurized Nanoparticle $\text{Bi}_2\text{Ba}_2\text{Tb}_{0.5}\text{Cu}_2\text{O}_{4+y}$

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Abstract. Previous researches on underdoped and overdoped Bi-2212 superconductor have shown that its mechanism follows the polarons-bipolarons theory of superconductivity. In this study, a chemically pressurized Bi-2212 compounds was synthesized and characterized. It was observed that phase analysis reveals the unique route of electron flow within the polycrystalline sample. The transmission electron microscopy (TEM) shows the presence of static and dynamic localizations that proves the possibly presence of Bose-Einstein condensation of inter-site bipolarons. This study on chemically pressurized $\text{Bi}_2\text{Ba}_2\text{Tb}_{0.5}\text{Cu}_2\text{O}_{4+y}$ compound has shown that the generation and dynamics of polarons and bipolarons are associated to the pentavalent post-transition nature of bismuth.

1. Introduction

Superconductivity of a material can be described as the state at which all the magnetic field lines within the material are completely expelled and its internal resistance is reduced to zero. A man named Kammerligh Onnes first discovered it in 1911, this type of superconductor was referred to as low temperature superconductor [1]. In 1986, George Bednorz and Alex Mueller discovered the high-temperature superconductor (HTS) [2]. The discovery of HTS sparked renewed interest to determine HTS, which resulted in the discovery other of superconductors such as yttrium-based superconductor, bismuth-based superconductor, thallium-based superconductor, mercury-based superconductor etc. The superconducting properties of the cuprates structure are dependent on the electrons moving along within the weakly-coupled layers of copper-oxide, which are bound to their filler layers by Van der Waal's forces [3-4].

Bismuth-based HTS have the empirical formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+x}$ (where $n=1,2,3$) and are reported to possess higher critical temperature than the lanthanum and yttrium cuprates superconductor (Figure 1) [5]. Thus Bi-2201 can be created when $n = 1$ compound ($\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$), Bi-2212 is created when $n = 2$ compound ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$), and Bi-2223 is created when $n = 3$ compound ($\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$). Other properties of cuprates includes: resistant to water and humidity; compositional stability; and it is highly ductile [6]. The ductility of bismuth cuprates has been utilized for texturing, tape-casting, flexible wire and superconducting tape magnet for high-speed magnetic-levitation (maglev) trains [7-8].

The bismuth based cuprates are of three major phases i.e., $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (also known as Bi-2201), $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (also known as Bi-2212), and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (also known as Bi-2223). Bi-2201 possesses a tetragonal crystal structure consisting of two sheared crystallographic unit cells and one CuO_2 (cuprates) plane [9]. It has double Bi-O planes stacked in such a way that the Bismuth atom of one plane sits below the Oxygen atom of the following consecutive plane. Here, the Cu atom forms an



octahedral coordination with respect to the oxygen atom in the structure. Bi-2212 possesses a tetragonal crystal structure with two CuO_2 planes. It also has double Bi-O planes. The coordination of the Cu atom is different in this phase, in that five oxygen atoms surround the Cu atom in a pyramidal arrangement. Bi-2223 has the highest superconducting temperature of the three Bismuth cuprates.

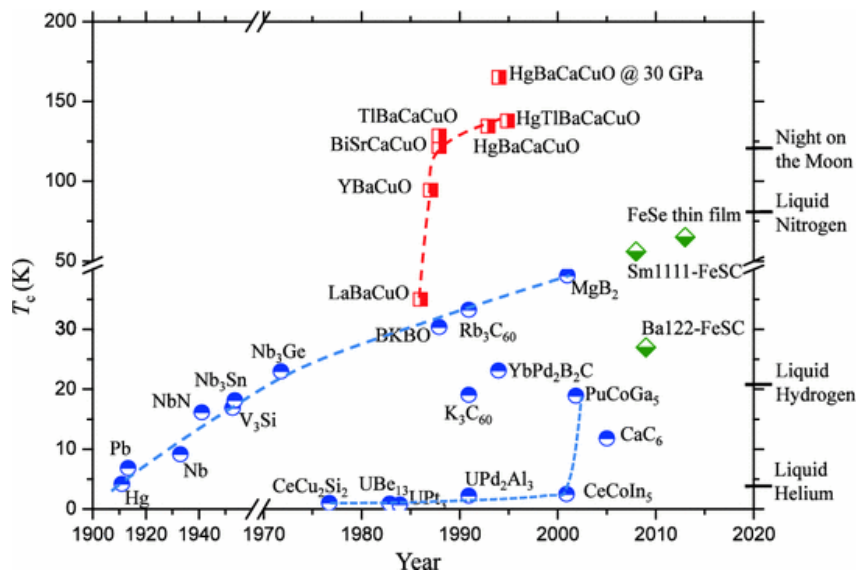


Figure 1. Critical temperature progression of superconductors [5]

The critical temperatures of the three types of Bismuth cuprates superconductor are presented in Table 1.

Table showing the Critical Temperatures (T_c) and who discovered the phase

Serial No.	Superconductor	Critical Temperature
1	Bi-2201	20K [10]
2	Bi-2212	90K[11], 96K [13]
3	Bi-2223	110K [12], 108K [13]
4	Bi-2234	104K [14]

The main scientific challenge in the bismuth cuprates is that Bi-2212 is yet to achieve the structural perfection and purity that YBCO possesses. In this study we perform chemical pressurization of the lattice to attain stability via manipulating the superconducting and non-superconducting planes. This idea was borne by substituting the strontium- $5s^2$ with barium- $6s^2$ (both are alkaline earth metal), calcium- $4s^2$ with terbium- $6s^2$ (i.e. changing an alkaline earth metal with rare earth metal). The terbium was given half of its stoichiometry to form $\text{Bi}_2\text{Ba}_2\text{Tb}_{0.5}\text{Cu}_2\text{O}_{4+y}$. The s electrons are relatively easily ionized (removed from the atom), hence the chemically pressurized system is expected to act differently. Zhao [15] postulated using angle-resolved photoemission spectra to determine Bose-Einstein condensation of inter-site bipolarons in underdoped Bi-2212. Hence, Bose-Einstein condensation of inter-site bipolarons has been found in both overdoped [16] and underdoped Bi-2212. This research is conducted to confirm if bismuth or copper atoms remotely is responsible for the presence of inter-site bipolarons.

2. Methodology

There are currently two broad methods for preparing pellets of homogenous superconducting bismuth. They are listed as follows in order of popularity: solid-state thermochemical reaction, which involves the processes of mixing, calcination and sintering. The other method is the solution Chemistry

processes, which includes Coprecipitation, Freeze-Drying, and Sol-gel. The flowchart of the methods is presented in Figure 2. The detail of the method is described in ref [17-18]

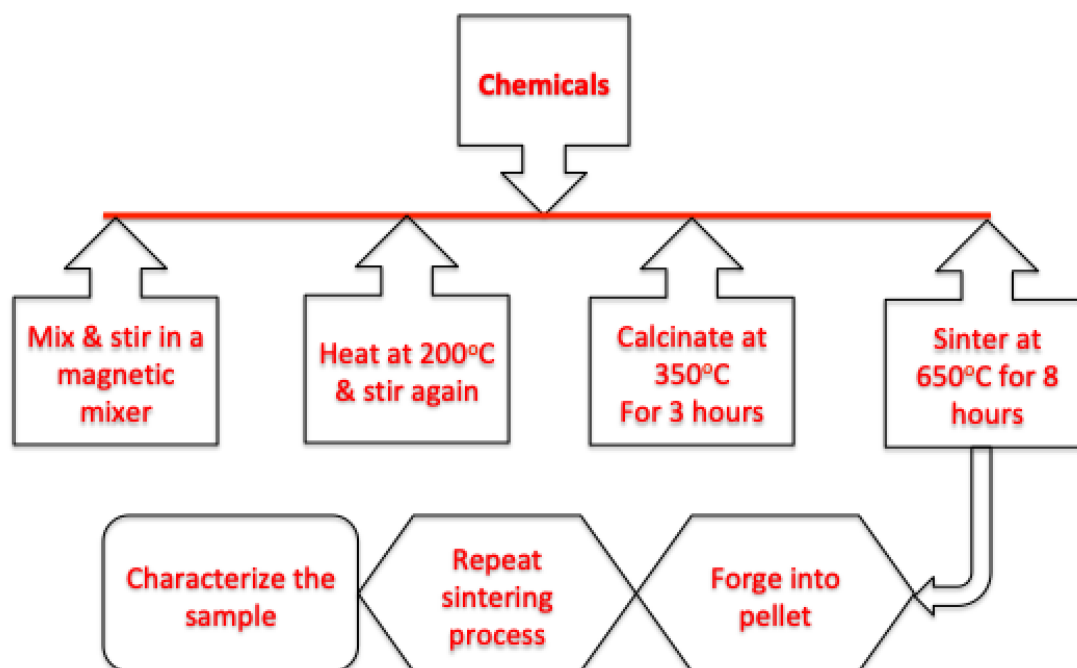


Figure 2. Flowchart of methodology

3. Results and Discussion

The XRD experiment was using the crystallography information file of the $\text{Bi}_2\text{Ba}_2\text{Tb}_{0.5}\text{Cu}_2\text{O}_{4+y}$ at a wavelength of 0.1540 nm, from 5 to 50° in a 2θ scale. The step size of 0.1°/min was used to obtain patterns with low noise. Six distinct peaks were observed at planes (002), (115), (0 0 10), (117), (200), and (0 0 12) and their corresponding d-spacing and structure F as (15.6Å, 802), (3.33Å, 476.5), (3.11Å, 1686.7), (2.95Å, 869.94), (2.79Å, 1387.9), and (2.6Å, 1704.9). There were also fourteen minor peaks i.e., (004), (006), (111), (008), (113), (020), (022), (202), (024), (204), (119), (026), and (206). From the main peaks it can be inferred that the polycrystalline compound had unusual orientations judging from the d-spacing and structure F(hkl). For example, phase analysis revealed that the internal structure of polycrystalline have higher electron density at (0 0 12), (0 0 10), and (200) planes. In like manner, the highest peak showed lower electron density. Only minor planes (111) and (115) had significant electron density function as the main peaks. The phase analysis shows that electron flow through the crystals would be characterized by certain grain boundaries. Based on the above revelation, the transmission electron microscopy (TEM) measurement of the sample is presented in Figure 4. The computational analysis of the TEM via the particulates distribution is presented in Figure 5. It is clear that there is a localization of particulates with green-yellowish boundaries. The boundaries are of different sizes. Inside the boundaries, there are groups of yellow peaks in the midst of red plain.

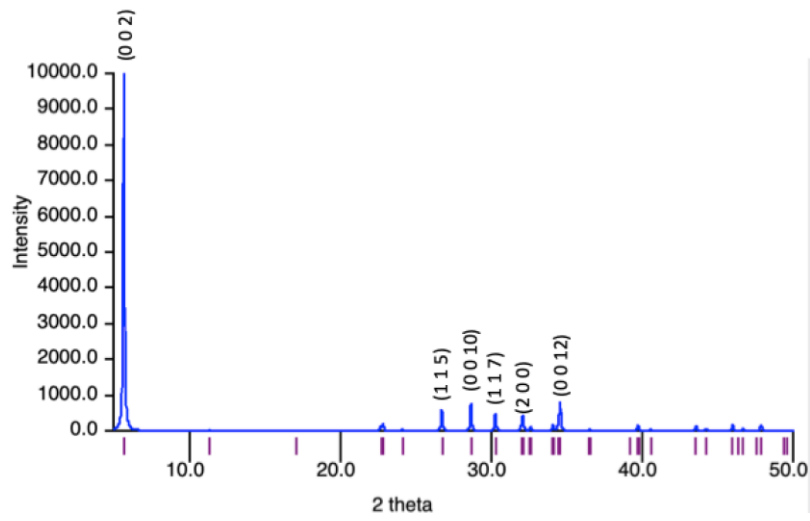


Figure 3. Plane analysis of an XRD measurement

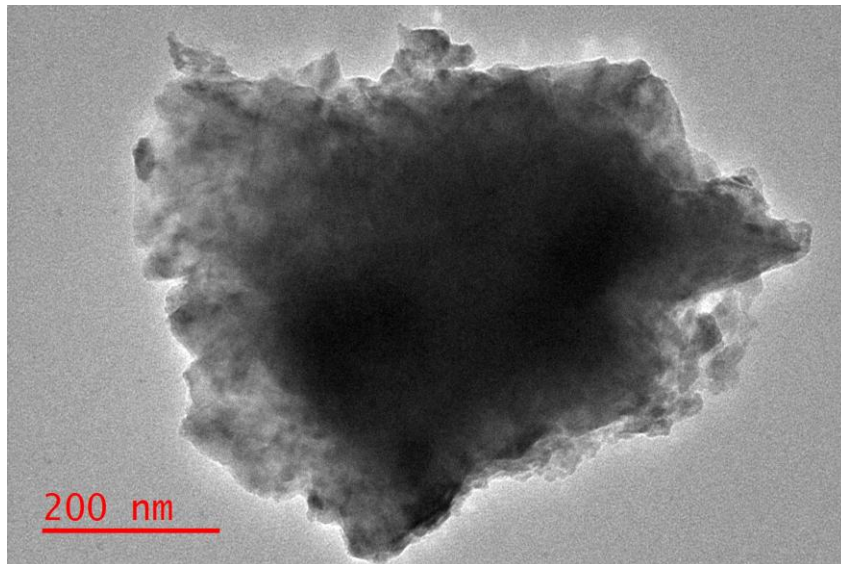


Figure 4. Internal atomic analysis using TEM

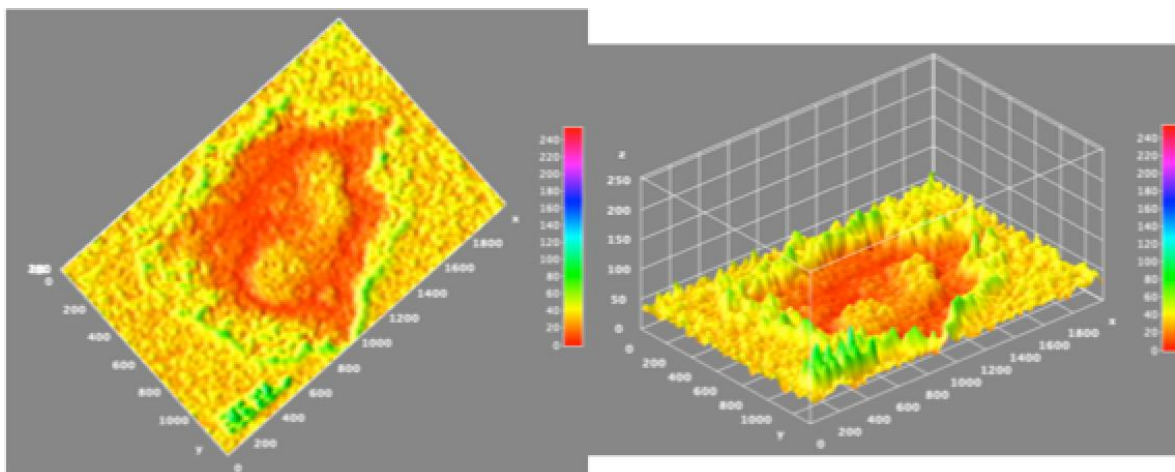


Figure 5. Particulate distribution in the TEM image

The sections of the yellow plains are somewhat divided into two. It is believed that under higher or lower temperatures, the shapes will change. This description fits into the idea of static and dynamic localization that generates polarons, as postulated in ref [19]. Considering the anomalies of electron transport through the different electron density region, and the new understanding of the localized regions in the compound, it is easy to infer that there would be a transition from itinerant (intersite) to bound immobile (onsite) bipolarons as postulated in ref [20]. Next we consider the size distribution of particulates as presented in Figure 6.

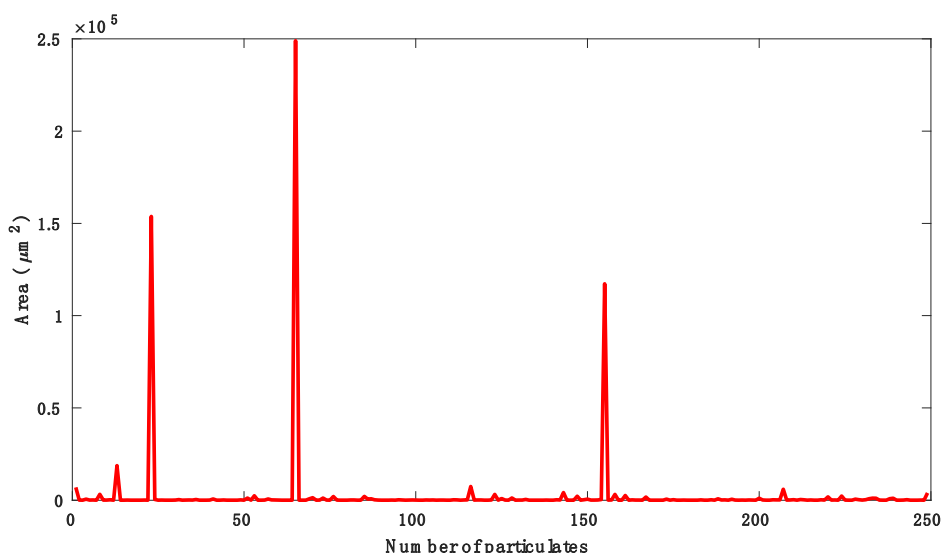


Figure 6. Particle size distribution of $\text{Bi}_2\text{Ba}_2\text{Tb}_{0.5}\text{Cu}_2\text{O}_{4+y}$

It is seen that there are four main sized particles that may likely represent the bismuth, barium, copper and terbium. In another perspective, the dynamics of the larger particulates are bound by the smaller particulates. This idea still supports the fact there are static and dynamic localizations that are good avenues for the generation of polarons. Hence, the concept of polarons and bipolarons are closely related to Bi-2212 structure.

4. Conclusion

Polarons and dipolarons have been previously reported in underdoped and overdoped Bi2212 superconductors. This study on chemically pressurized $\text{Bi}_2\text{Ba}_2\text{Tb}_{0.5}\text{Cu}_2\text{O}_{4+y}$ compound has shown that the generation and dynamics of polarons and bipolarons are associated to the pentavalent post-transition nature of bismuth. This result means that the mechanism of the Bi-2212 associated compounds will naturally generate polarons and bipolarons. The study has strongly supported the polarons-bipolarons superconductivity theory.

5. Acknowledgments

The authors appreciate the partial sponsorship of Covenant University.

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