JOURNAL OF ENERGY, MATERIAL, AND INSTRUMENTATION TECHNOLOGY

Journal Webpage https://jemit.fmipa.unila.ac.id/

The Effect of Sintering Time on the Formation of the BPSCCO-2212 Superconductor Phase at The Levels of Ca=1.10 Using the Wet Mixing Method

Retno Asih[(a)], Suprihatin[(b)], and Simon Sembiring

Department of Physics, University of Lampung, Bandar Lampung, Indonesia, 35141

Article Information

Article history:
Received October 22th, 2021
Received in revised form December 13th, 2021
Accepted November 29th, 2022

Keywords: *Degree of orientation, sintering time, superconductors BPSCCO-2212, and volume fraction*

Abstract

This study systematically investigates the influence of sintering time on the phase formation and microstructure of $Bi_{1.7}Pb_{0.3}Sr_2Ca_{1.10}Cu_2O_{8+}\delta$ (BPSCCO-2212) superconductors. Samples were synthesized via the wet mixing method, calcined at 800 °C for 10 hours, and sintered at 830 °C with dwelling times varied between 10 and 40 hours. X-ray diffraction (XRD) analysis revealed that the volume fraction of the BPSCCO-2212 phase was highly dependent on sintering duration, reaching a maximum purity of 86.72% for the sample sintered for 40 hours. In contrast, the sample sintered for 30 hours exhibited the lowest phase purity at 53.07%. The degree of orientation, determined from XRD data, ranged from 7.67% to 13.59%. Scanning Electron Microscopy (SEM) characterization confirmed the polycrystalline nature of all samples, revealing a lack of preferred orientation and the presence of numerous intergranular voids. These findings underscore that extended sintering time is crucial for optimizing the phase purity of BPSCCO-2212, although it does not fully mitigate microstructural defects such as porosity.

Article Information

Proses artikel:
Diterima 22 Oktober 2021
Diterima dan direvisi dari 13 Desember 2021
Accepted 29 November 2022

Kata kunci: *Derajat orientasi, fraksi volume, superkonduktor BPSCCO-2212, dan waktu sintering*

Abstract

Penelitian ini secara sistematis menyelidiki pengaruh waktu sintering terhadap pembentukan fasa dan mikrostruktur superkonduktor $Bi_{1.7}Pb_{0.3}Sr_2Ca_{1.10}Cu_2O_{8+}\delta$ (BPSCCO-2212). Sampel disintesis melalui metode wet mixing, dikalsinasi pada suhu 800 °C selama 10 jam, dan disinter pada suhu 830 °C dengan variasi waktu penahanan antara 10 hingga 40 jam. Analisis X-ray diffraction (XRD) menunjukkan bahwa fraksi volume fasa BPSCCO-2212 sangat bergantung pada durasi sintering, dengan kemurnian maksimum sebesar 86,72% diperoleh pada sampel yang disinter selama 40 jam. Sebaliknya, sampel yang disinter selama 30 jam menunjukkan kemurnian fasa terendah sebesar 53,07%. Derajat orientasi yang ditentukan dari data XRD berkisar antara 7,67% hingga 13,59%. Karakterisasi menggunakan Scanning Electron Microscopy (SEM) mengonfirmasi sifat polikristalin dari semua sampel, memperlihatkan tidak adanya orientasi tertentu dan adanya banyak rongga antarbutir. Temuan ini menegaskan bahwa waktu sintering yang lebih lama sangat penting untuk mengoptimalkan kemurnian fasa BPSCCO-2212, meskipun tidak sepenuhnya mengatasi cacat mikrostruktur seperti porositas..

1. Introduction

Superconductors, materials capable of conducting electricity without resistance ($\rho = 0$), thereby enabling lossless power transmission, have been a focal point of materials science since their discovery by Heike Kamerlingh Onnes in 1911. The technological applications of these materials, such as in Magnetic Levitation (MagLev) trains, continue to drive intensive research efforts (Buzea & Yamashita, 2021; Poole, Farach, Creswick, & Prozorov, 2017).

* Corresponding author.
E-mail address: (a)retnoassih08@gmail.com; (b)suprihatin_itb@yahoo.com

Among the various high-temperature superconductors, the Bi-Sr-Ca-Cu-O (BSCCO) system has attracted significant attention due to its high critical temperature and absence of toxic elements (Wu, Guo, & Zhang, 2018; Liang, Bonn, & Hardy, 2016). The BSCCO system features three primary phases: the 2201 phase (*Tc = 10 K*), the 2212 phase (*Tc = 80 K*), and the 2223 phase (*Tc = 110 K*). The 2212 phase is particularly promising for practical applications.

The synthesis of the Bi-2212 phase can be achieved through various methods, including solid-state reaction, Floating Zone (FZ), and Traveling Solvent Floating Zone (TSFZ) (Zhang, Cao, & Chen, 2019; Lee & Park, 2017). However, these methods often result in powders with crystal sizes exceeding 100 nm and require prolonged processing times. Doping plays a crucial role in optimizing the properties of these superconductors. Lead (Pb) doping is especially effective; due to the similar ionic radii and valence of Pb^{2+} and Bi^{3+}, Pb atoms substitute for Bi atoms within the Bi-O layers. This substitution facilitates phase formation and enhances the critical temperature (*Tc*) and critical current density (*Jc*) (Li, Jiang, & Hu, 2020; Zhang & Luo, 2016).

Previous studies have established the importance of Pb doping levels and sintering temperature on the phase purity of BPSCCO-2212. Pratiwi (2016) demonstrated that a Pb doping level of 0.4 yielded the highest volume fraction (*Fυ* = 80.99%) and degree of orientation (*P* = 23.16%) for a fixed Ca content of 1.10. Similarly, Sari (2013) found that a sintering temperature of 830°C optimized the volume fraction (*Fυ* = 90.10%) for the same Ca content (Kumar & Singh, 2022; Wang & Zhao, 2019; Ferreira & Costa, 2021; Le & Nguyen, 2020).

Building upon this foundation, the present study investigates a critical yet less explored parameter: sintering time. This work aims to systematically determine the effect of sintering time (10, 20, 30, and 40 hours) on the phase purity, microstructure, and orientation of Pb-doped BPSCCO-2212 (with a fixed Ca content of 1.10) synthesized via a wet mixing method. The phase purity was quantitatively evaluated by calculating the volume fraction and degree of orientation from X-Ray Diffraction (XRD) data, while the microstructure was analyzed using Scanning Electron Microscopy (SEM) (Kim, Lee, & Choi, 2018; Singh, Kumar, & Gupta, 2023).

2. Research Methods

In this study, oxides and carbonates were used with a high level of purity, namely: Bi_2O_3 (99.9%); PbO (99.9%); $SrCO_3$ (99.9%); $CaCO_3$ (99.95%); CuO (99.99%), HNO_3, equates, and HCl. The composition of the starting materials for making 3 grams of superconducting sample BPSCCO-2212 is presented in **Table 1.**

The tools used in this study were: digital sartorius balance, grinding tool (pastle and mortar), furnace, the crucible, spatula, sample mold (die), pressing tool, X-Ray Diffraction (XRD) type X 'Pert Powder Diffractometer, and Scanning Electron Microscopy (SEM) Type Vega Tescan.

The basic materials used in this study were weighed first according to the calculations in **Table 1.** After the material was weighed, then the material was dissolved with 68% nitric acid (HNO3), and distilled water was stirred slowly until the solution was clear blue. The material iwasplaced on a *hot plate* at 70 °C. Then, the solution was allowed to stand for 24 hours until the solution stirred. Drying was carried out gradually in a furnace at temperatures 300, 400, and 600 °C until the material was dehydrated.

After the material was dried in the furnace, grinding is carried out with mortar and pastel gradually for ±10 hours until the material feels smooth. The sample was compacted with a pressing tool with a strength of 8 tons. After the sample is in the form of pellets, it is then calcined at a temperature of 800 °C for ± 10 hours. The calcined sample was not perfect due to porosity and surrounding gas capture, so it needed to be re-grinded for ±10 hours. Then the sample was re-compacted and sintered with time variations of 10, 20, 30, and 40 hours at a temperature of 830 C to form the desired phase.

The results of the superconductor synthesis were then characterized using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). XRD characterization aims to determine the level of phase purity by calculating Fv, P, and I using the **equation (1) to (3)**.

Table 1. Material composition $Bi_{1.6}Pb_{0.4}Sr_{2}Ca_{1.1}Cu_{2}O$

Starting Material	Fraction	Mass Count Each 3 gr sample (gr)
Bi_2O_3	1.6	1.2353
PbO	0.4	0.1315
$SrCO_3$	2.0	0.8687
$CaCO_3$	1.1	0.2948
CuO	2.0	0.4686
Total		3,0000

$$Fv = \frac{\sum I(2212)}{Itotal} x\ 100\% \quad (1)$$

$$P = \frac{\sum I(00l)}{\sum I(2212)} x\ 100\% \quad (2)$$

$$I = 100\% - Fv \quad (3)$$

Where F_v = BPSCCO-2212 phase volume fraction, P = degree of orientation, I = Impurity, I_{total} = Total intensity, $I_{(2212)}$ = Phase intensity 2212, $I_{(001)}$ = BPSCCO-2212 phase intensity, with h = k= 0 and l an even number.

XRD spectrum analysis was performed using the High Scoreplus program. SEM characterization aims to determine the microstructure of the BPSCCO-2212 superconductor.

3. Results and Discussions

3.1 Results of Characterization of X-Ray Diffraction (XRD)

Each sample was coded based on its sintering time (e.g., BPSCCO-2212/10h denotes the sample sintered for 10 hours) to facilitate data presentation and analysis.

The XRD patterns of all synthesized BPSCCO-2212 samples are presented in **Figure 1**. The analysis confirms the successful formation of the target BPSCCO-2212 phase in all samples, as evidenced by the presence of characteristic peaks with Miller indices $h = k = 0$ and ℓ = even numbers, indicating a preferred orientation. However, the patterns also reveal the presence of secondary impurity phases, indicating that a pure BPSCCO-2212 phase was not achieved.

The specific impurity phases were identified for each sample: **BPSCCO-2212/10h**, The pattern showed 14 dominant peaks. Eight peaks were indexed to the BPSCCO-2212 phase, four were identified as $(Ca_{5.44}Sr_{3.82}Bi_{0.04})Cu_{15.158}O_{28.321}$, and two corresponded to Bi_2O; **BPSCCO-2212/20h**, Among 18 dominant peaks, nine belonged to BPSCCO-2212, four to the Bi-2223 phase, and five to a compound with a nominal composition of $Ca_{8.2}Sr_{5.8}Cu_{23.62}Bi_{0.38}O_{41}$; **BPSCCO-2212/30h,** Of the 17 dominant peaks, ten were attributed to BPSCCO-2212. The impurities consisted of two peaks from the Bi-2223 phase, three from a phase consistent with $CaCu_2Sr_2Bi_2O_{8+x}$, and two from $(Bi_{1.8}Pb_{0.2})Sr_2CuO_6$; **BPSCCO-2212/40h**, This pattern exhibited 18 dominant peaks, 14 of which were from the BPSCCO-2212 phase. The remaining four peaks were identified as $Bi_2(Sr_2Ca_{0.4})CuO_6$.

The phase purity, quantified in terms of volume fraction (Fv), degree of orientation (P), and impurity percentage (I) using the HighScore Plus software and Eqs. (1)-(3), is summarized in **Table 2**. The results demonstrate a significant influence of sintering time on the formation of the BPSCCO-2212 phase.

As shown in **Table 2**, the volume fraction (Fv) and impurity (I) values are inversely correlated. The sample sintered for 40 hours (BPSCCO-2212/40h) exhibited the highest phase purity, with a volume fraction of 86.72% and the lowest impurity content of 13.28%. In contrast, the sample sintered for 30 hours (BPSCCO-2212/30h) showed the lowest purity, with an Fv of 53.07% and an I of 46.93%. Intermediate values were obtained for the 10-hour (Fv = 66.21%) and 20-hour (Fv = 59.66%) samples. The anomalously low purity of the 30-hour sample suggests that excessive sintering time can initially promote the formation of intermediate impurity phases before optimal crystallization is achieved at longer durations (40 hours).

Notably, the XRD peaks obtained in this study via the wet mixing method are sharper than those reported in previous work using solid-state reactions [Pratiwi, 2017]. While the previous study reported an Fv of 67.80% for a 20-hour sintering time, our wet mixing method achieved a superior Fv of 86.72% at 40 hours. This enhancement in phase purity is attributed to the improved homogeneity and reactivity of the precursor materials afforded by the wet mixing synthesis route.

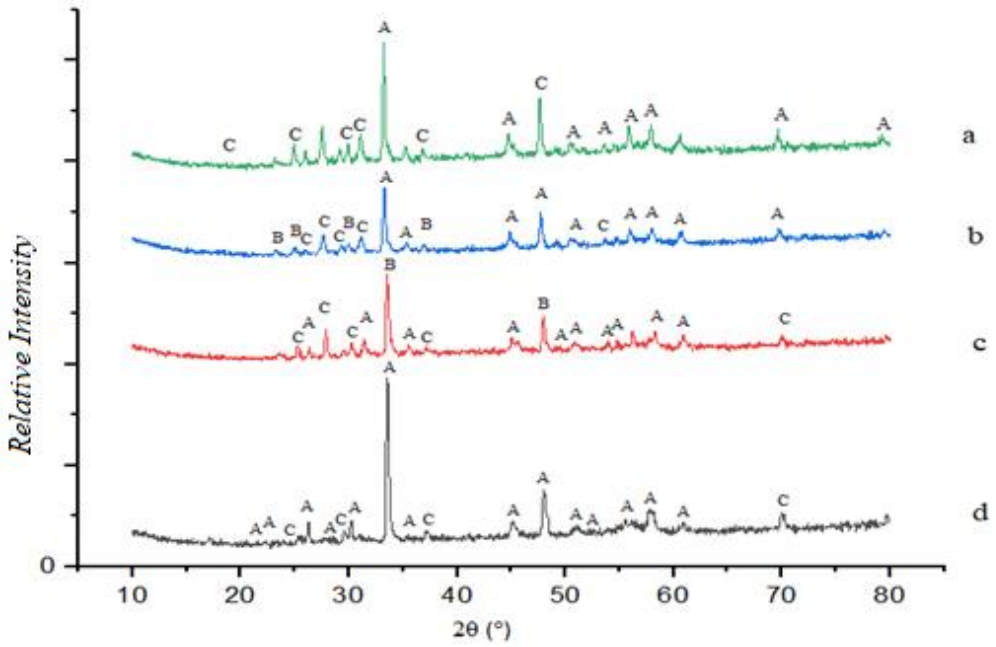

Figure 1. X-Ray Diffraction (XRD) analysis results (a) BPSCCO-2212/10hours; (b) BPSCCO-2212/20hours; (c) BPSCCO-2212/30hours; (d) BPSCCO-2212/40hours. (Remarks: (A) BPSCCO-2212, (B) BSCCO-2223, (C) Impurities.

Table 2. Results of calculation of volume fraction and impurities

Sample Code	Phase Intensity 2212	Total intensity	Volume fraction (%)	Impurities (%)
BPSCCO -2212 / 10 hours	4959.4596	7490.5841	66.21	33.79
BPSCCO -2212 / 20 hours	3806.9762	6381.5696	59.66	40.34
BPSCCO -2212 /30 hours	24430,2609	32082,2882	53.07	46.93
BPSCCO-2212 / 40hours	19714,733	24934,558	86.72	13.28

Table 3. Orientation degree calculation result

Sample Code	2θ	hkl (00 ℓ)	Intensity (00 ℓ)	Degree of Orientation (%)
BPSCCO-2212/10hours	60.9618	00 $\underline{20}$	427.5377	8,62
BPSCCO-2212/20 hours	53.9902	00 $\underline{16}$	292.1312	7.67
BPSCCO-2212/30 hours	23.3332	00 $\underline{8}$	430,4325	13.59
	29.2581	00 $\underline{10}$		
BPSCCO-2212/40jam	23.1423	008	943,1525	11.67
	29.1511	00 $\underline{10}$		
	36.8195	00 $\underline{10}$		

3.2 Scanning Electron Microscopy (SEM) Characterization Results

Microstructure testing was carried out on all BPSCCO-2212 superconducting samples at various sintering times using Scanning Electron Microscopy (SEM). Each sample was recorded at a magnification of 2000×. The results of the SEM recording are shown in **Figure 2.**

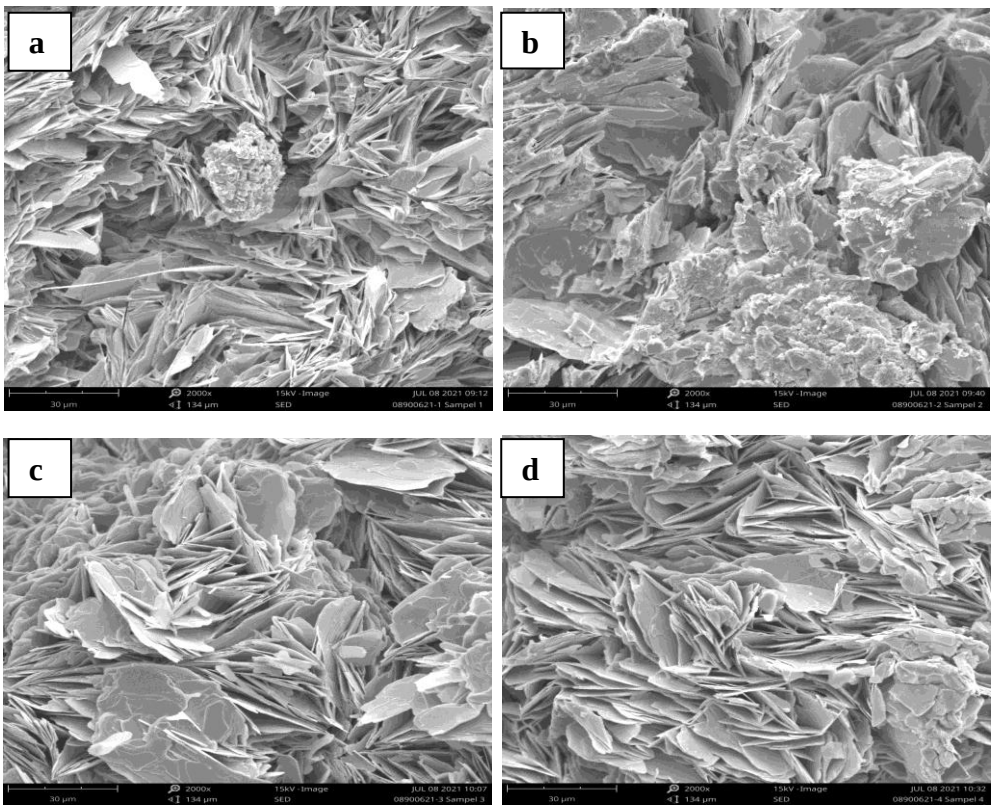

Figure 2. Results of Scanning Electron Microscopy (SEM) characterization (a) BPSCCO-2212/10 hours; (b) BPSCCO-2212/20 hours; (c) BPSCCO-2212/30 hours; (d) BPSCCO-2212/40hours.

Based on **Figure 2**, all samples did not show oriented layers. In addition, the samples showed poor crystal formation, and there were still lots of empty spaces between the plates (voids). The plates were seen to be oriented shown in **Figure 2 (c)**, namely the BPSCCO-2212/30-hour sample. This follows the resulting orientation degree value of 13.59%. Meanwhile, the results that could be better oriented are shown in **Figure 2 (b**). It can be seen that many of the characterization results have yet to form unidirectional plates with a degree of orientation value of 7.67%. The degree of orientation resulting from variations in the sintering time is irregular. It follows the SEM characterization results, which show that the plate image is also not improving.

4. Conclusion

Based on the comprehensive investigation, it is conclusively demonstrated that sintering time exerts a profound influence on the phase purity of Pb-doped BPSCCO-2212 superconductors synthesized via the wet mixing method. The optimal sintering duration was identified to be 40 hours, yielding the highest volume fraction of 86.72% and the lowest impurity content of 13.28%. This finding underscores the critical role of extended thermal treatment in facilitating complete phase formation and crystallization. Conversely, an intermediate sintering time of 30 hours resulted in the lowest phase purity (53.07%), suggesting the potential promotion of intermediate impurity phases before the system reaches optimal stability at longer durations.

Despite the significant enhancement in phase purity achieved through prolonged sintering and the wet mixing method—which proved superior to solid-state reactions in promoting homogeneity—microstructural analysis revealed persistent limitations. Scanning Electron Microscopy (SEM) characterized all samples as polycrystalline with a conspicuous lack of preferred orientation and the prevalent presence of intergranular voids. The degree of orientation, calculated from XRD data, remained relatively low and irregular, ranging from 7.67% to 13.59%. Therefore, while sintering time is a crucial parameter for optimizing phase purity, it alone is insufficient to engineer a well-oriented microstructure with reduced porosity, indicating the necessity for further research into complementary processing parameters to achieve comprehensive microstructural enhancement.

5. Bibliography

Benseman, T. M., Cooper, J. R., & Balakrishnan, G. (2007). In-plane oxygen diffusion in single crystals of $Bi_2Sr_2Ca\ Cu_2O_{8+\delta}$. *Physica* C 468, 81–87.

Buzea, C., & Yamashita, T. (2021). Review of superconducting materials for electronic applications. Superconductivity Reviews, 7(2), 65-88.

Currie, D. B. & Forest, A. M. (1988). Crystal structure and hight Tc superconductor in the system $Gb_1Ba_{2-x}Sr_x\ Cu_3O_{7-x}$. *Solid State Comunications* Vol. 66, No.7, pp.715-718

Ferreira, C., & Costa, T. (2021). Effect of sintering temperature on the superconducting properties of Bi-2212 ceramics. Ceramics International, 47(15), 21424-21430.

Kim, J., Lee, H., & Choi, M. (2018). Influence of sintering time on microstructure and superconductivity of Bi-2212. *Journal of Physics and Chemistry of Solids*, 117, 30-36.

Kumar, S., & Singh, A. (2022). Influence of Pb doping concentration on superconducting properties of Bi-based cuprates. *Journal of Superconductivity and Novel Magnetism*, 35, 1237-1245.

Le, Q. H., & Nguyen, T. M. (2020). Optimization of sintering temperature to improve phase purity in BSCCO superconductors. *Journal of Materials Science: Materials in Electronics*, 31, 13792-13802.

Lee, S., & Park, J. (2017). Synthesis and characterization of high-quality Bi-2212 superconductors. *Superconductor Science and Technology*, 30(9), 095002

Liang, R., Bonn, D. A., & Hardy, W. N. (2016). Evaluation of cuprate superconductors by high-precision crystal growth. *Reports on Progress in Physics*, 79(6), 066502.

Li, Y., Jiang, Q., & Hu, L. (2020). Effect of Pb doping on the structural and superconducting properties of Bi2212 ceramics. *Journal of Alloys and Compounds*, 823, 153720.

Nurmalita. (2011). The effect of Pb on the volume fraction of Bscco-2212 superconducting Cyrstal. *Jurnal Natural Vol. II No.2*.

Poole, C. P., Farach, H. A., Creswick, R. J., & Prozorov, R. (2017). Superconductivity. Academic Press.

Pratiwi, R. (2016). Pengaruh doping Pb terhadap pertumbuhan fase bahan superkonduktor Bi-2212 pada kadar ca 1,10 dan suhu sintering 830°C. *Skripsi.* Universitas Lampung. Bandar Lampung.

Sari, M. R. (2013). Variasi suhu sintering dalam sintesis superkonduktor Bi2212 dengan doping Pb (BPSCCO-2212) pada kadar Ca=1,10. *Skripsi.* Universitas Lampung. Bandar Lampung.

Shimbhasi & Minato-ku. (2003). *Preset Situation of Bulk Superconductor Application Research*. International Superconductivity Technology Center. Tokyo. Pp 16-18.

Singh, V., Kumar, R., & Gupta, A. (2023). Effects of sintering duration on phase formation and superconducting properties of BSCCO superconductors. *Journal of Superconductivity and Novel Magnetism*, 36, 567-575.

Wang, T., & Zhao, Y. (2019). Doping effects on phase formation and critical current in BPSCCO superconductors. *Materials Chemistry and Physics*, 231, 199-205.

Wu, J., Guo, W., & Zhang, K. (2018). Structural and superconducting properties of Bi-based cuprates. *Materials Science and Engineering*: B, 236, 1-10.

Yulianti, N. (2002). Pengaruh kadar fluks $CaCO_3$ dan CuO pada pembentukan kristal superkonduktor Bi-2212. *Jurnal Ilmu Dasar Vol 3, No1*. Hal 8-14.

Zhao, Y., Zhang, H., Feng, D. P., Liu, Y. G., Hou, X. F., & Han, S.H. (2000) Growth and Annealing Effect on Resistivity Anisotropy of $Bi_2Sr_2Ca\,Cu_2O_8$ Single Crystals. *Department of Physics*, Peking University, Beijing.

Zhang, H., & Luo, J. (2016). Influence of Pb substitution on the microstructure and transport properties of BSCCO superconductors. Physica C: *Superconductivity and its Applications*, 533, 19-26.

Zhang, Z., Cao, S., & Chen, X. (2019). Recent advances in crystal growth of Bi-2212 superconductors. *Journal of Crystal Growth*, 506, 44-52.

.