*Solid State Science and Technology, Vol. 31, No. 2 (2023), 63-70*
*https://doi.org/10.66514/ssst31-2-63-70*

# EFFECT OF ANNEALING TEMPERATURE CONDITION ON THE PHASE FORMATION AND ELECTRIC PROPERTIES OF $YBa_2Cu_3O_{7-\delta}$ SUPERCONDUCTOR SYNTHESISED BY THERMAL TREATMENT METHOD

*Fatma Barood[1], Mohd Mustafa Awang Kechik[1,*], Muralidhar Miryala[2], Chen Soo Kien[1], Lim Kean Pah[1], Abdul Halim Shaari[1], Hussein Baqiah[3]*

*[1]Laboratory of Superconductor & Thin Films, Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia*

*[2]Materials for Energy and Environmental Laboratory, Superconducting Materials Shibaura Institute of Technology, 3 Chome-7-5 Toyosu, Koto, Tokyo 135-8548, Japan*

*[3]Shandong Key Laboratory of Biophysics, Institute of Biophysics, Dezhou University, No. 566 University Rd. West, Dezhou, Shandong, China*

Received: 2 January 2024; Accepted: 10 February 2024

** Correspondence author; Email: mmak@upm.edu.my*

## ABSTRACT

The current study reports on the effect of annealing temperature on the phase formation and electrical properties of $YBa_2Cu_3O_{7-\delta}$ superconductor synthesised by thermal treatment technique. The specimens were separated into sets A, B, and C. The sets A and B were sintered at 980 °C for 24 h and then exposed to additional annealing at 650 °C and 500 °C for 12 h, respectively, during the sintering process while being cooled down to room temperature under oxygen flow. The set C was only sintered at 980 °C for 24 h in oxygen flow and without annealing. All prepared samples were analysed by X-ray diffraction (XRD) technique, field-emission scanning electron microscope (FESEM) and four-point probe measurement. The structural examination via the XRD technique showed an orthorhombic crystal structure with the main phase of $YBa_2Cu_3O_{7-\delta}$ for all samples, besides a small amount of $YBa_2Cu_3O_{7-\delta}$ as a secondary phase for samples B and C. According to the findings of the FESEM examination, the annealing of the samples caused an increase in the average grain size of the samples. The temperature-resistivity measurements showed that all samples exhibited metallic behaviour in the normal state with a high critical transition temperature (95.6 K) obtained after annealing at 650 °C for set A. Thus, the experimental results showed that further annealing at 650 °C may be the optimal heat treatment temperature for producing $YBa_2Cu_3O_{7-\delta}$ superconductors with better superconducting properties.

*Keywords: $YBa_2Cu_3O_{7-\delta}$ superconductor; thermal treatment,; annealing temperature; superconducting properties*

## INTRODUCTION

The $YBa_2Cu_3O_{7-\delta}$ (Y123) was discovered as the first high-$T_c$ superconductor in the late 1980s, with a critical transition temperature surpassing the boiling point of liquid nitrogen [1]. The $YBa_2Cu_3O_{7-\delta}$ material has attracted significant interest across various fields of research, from fundamental to applied studies. Considerable attempts and efforts have been directed towards the synthesis of superconducting materials of $YBa_2Cu_3O_{7-\delta}$ with optimum morphology and physical properties while maintaining the highest possible level of purity. The production of the $YBa_2Cu_3O_{7-\delta}$ superconductor is commonly achieved through the solid-state reaction [2]–[4] or wet routes, including co-precipitation [5]–[7] and sol-gel [8]–[10].

Recently, Dihom et al. [11] reported a new thermal treatment method that involves the use of high-purity metal nitrate powders as starting materials and polyvinyl pyrrolidone (PVP) as a capping agent. In addition to its cost-efficiency, simplicity of use, and environmentally-friendly, this synthesis method also offers the advantage of achieving homogeneous products and fine grain sizes [12-14]. Accordingly, several studies have been conducted on the fabrication of superconducting $YBa_2Cu_3O_{7-\delta}$ specimens by employing the thermal treatment method [15-19]. The properties of superconducting materials can be improved by heat treatment processes, including calcination, sintering, and annealing. It is known that microstructure, crystal formation and sample densification can be altered by heat treatment conditions. Accordingly, during the preparation of target materials, it was observed that the superconducting transition temperature $T_c$ of these compounds showed a significant dependence on their oxygen content. This dependence can be controlled by modifying the annealing temperature. Such behaviour was shared by several other groups [20, 21].

In this work annealing at 500 °C and 650 °C were chosen to promote the formation of the desired $YBa_2Cu_3O_{7-\delta}$ phase. This temperature is within the range that allows the precursors or starting materials to react and transform into the superconducting phase while minimizing the formation of unwanted secondary phases [22, 23]. Along with this finding, further study into the annealing process is essential. Therefore, it is important to develop an optimal additional oxygenation annealing process at low temperatures (500 - 650 °C) in an oxygen rich environment to restore the oxygen stoichiometry and superconducting properties. The aim of this paper was to investigate the influence of annealing on the structure and superconducting properties of the $YBa_2Cu_3O_{7-\delta}$ superconductor fabricated by the thermal treatment method.

## EXPERIMENTAL DETAILS

A thermal treatment approach similar to that described by Dihom et al. [20] was used to produce $YBa_2Cu_3O_{7-\delta}$ powder. To make an aqueous solution of metal nitrates, stochiometric amounts of $Y(NO_3)_2.6H_2O$, Ba $(NO_3)_2$, and Cu $N_2O_6.2.5H_2O$ were dissolved in 300 ml of deionised water. 6 g of polymer (PVP) was added to the mixture before stirring and heating it at 80 °C for 2 h with a magnetic stirrer. To evaporate the water, the solution was dried in an oven at 110 °C for 24 h. The dried, solid green gel was ground in a mortar for 1 h to make a fine powder before being subjected to the first calcination at 600 °C for 4 h. The resulting powder was ground for 15 min before being calcined at 910 °C for 24 h. The obtained mixture was ground and pressed into 13 mm diameter pellets using a hydraulic press under a pressure load of three tonnes. The pellets were divided into three sets, namely, A, B and C. The three sets were sintered at 980 °C

for 24 h, with further annealing subjected to sets A and B at 650 °C and 500 °C for 12 h under oxygen flow, respectively. Whereas the set C was only sintered at 980 °C for 24 h in flowing $O_2$ without annealing.

The powder samples were analysed for phase composition and crystal structure using an X-ray diffractometer (XRD, Xpert Pro Panalytical Philips DY 1861), with peak positions ranging from 20° to 70°. The surface morphology and elemental composition of the sample were analysed using a field emission scanning electron microscope (FESEM) and an energy-dispersive X-ray spectrometer (EDX). The determination of the superconducting transition temperature ($T_c$) was carried out using the four-probe method.

## RESULTS AND DISCUSSION

Figure 1 depicts typical X-ray patterns of sets A and B, annealed at 650 °C and 500 °C, respectively, and set C sintered at 980 °C without annealing. All indexed XRD diffraction peaks were related to a predominantly single phase with a perovskite-like $YBa_2Cu_3O_{7-\delta}$ structure and symmetry Pmmm 47. The $YBa_2Cu_3O_{7-\delta}$ phase formation, which is characteristic of the major intensity peaks (103) and (013), was confirmed in all sets, besides the presence of a minor quantity of secondary phase (indicated as $YBa_2Cu_3O_{7-\delta}$ in the figure) observed in sets B and C. It was observed that the intensity of XRD diffraction pattern peaks was higher for the annealed samples (sets A and B) than the sample without annealing (set C) and was the highest for the set A that annealed at 650 °C. This indicates that the annealing enhances crystal $YBa_2Cu_3O_{7-\delta}$ growth along the direction of the (00l) plane by increasing the annealing temperature. The measured lattice constants *a*, *b* and *c* are listed in Table 1. It can be noticed that there is no significant variation in lattice value constants *a* and *b*. Furthermore, the lattice constant *c* of sets B and C was higher than set A. Meanwhile, the orthorhombicity factor ($b$-$a$/$b$+$a$) of the $YBa_2Cu_3O_{7-\delta}$ phase is close to $7.3 \times 10^{-3}$ for all samples. The calculation of the oxygen content (7-δ) in $YBa_2Cu_3O_{7-\delta}$ samples was performed based on the *c*-axis lattice parameter, using the formula $7-\delta = 75.25-5.856c$ [24]. The process of annealing promoted a rise in the oxygen content by reducing the value of the lattice parameter *c*, which is typically associated with an increase in the oxygen content. [25]. The Debye-Scherrer formula was used to determine the average crystallite size by measuring the higher intensity peak of the (103) peak [26].

$$L = \frac{k\lambda}{\beta cos\theta} \tag{1}$$

where $L$ is the crystalline size, $k$ = (0.9), a numeric constant, $\lambda$ = (0.1542 nm), the wavelength of the incident x-rays, $\beta$ is the peak width at half maximum (FWHM) and $\theta$ is Bragg angle. The process of annealing promoted the growth of the crystalline size of the $YBa_2Cu_3O_{7-\delta}$ samples.

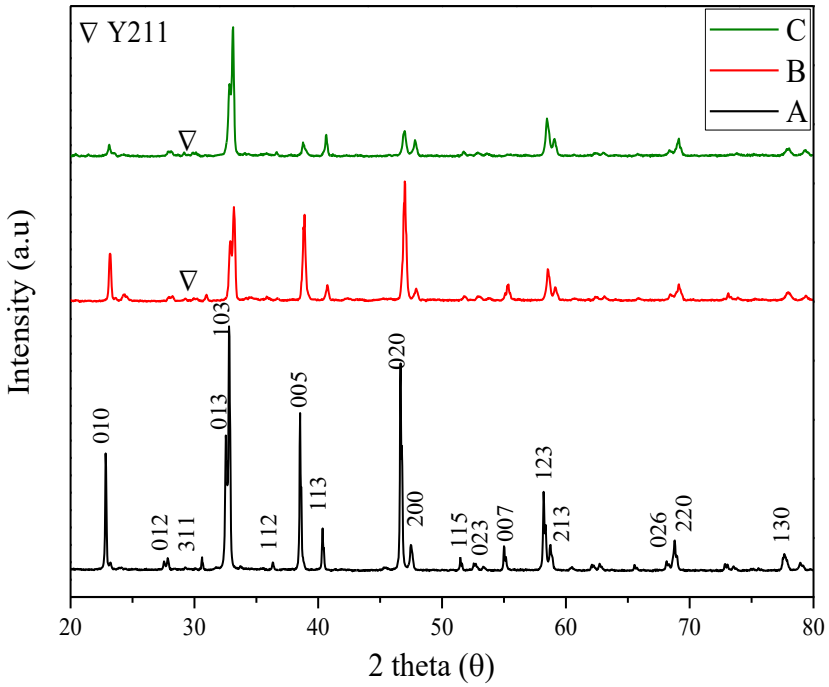


Figure 1. X-ray diffraction patterns of the $YBa_2Cu_3O_{7-\delta}$ samples: (A) annealed at 650 °C, (B) annealed at 500 °C and (C) without annealing

Table 1. Lattice constant *a*, *b*, and *c*, orthorhombicity, crystallite size, volume fraction and oxygen content of the $YBa_2Cu_3O_{7-\delta}$ samples A, B and C

| | *a* (Å) | *b* (Å) | *c* (Å) | Ortho-rhombicity ($10^{-3}$) | Crystallite size (nm) | Y123:Y211 volume fraction (%) | Oxygen content 7-δ |
|---|---|---|---|---|---|---|---|
| A | 3.827 | 3.885 | 11.672 | 7.520 | 180 | 100:0 | 6.89 |
| B | 3.827 | 3.883 | 11.687 | 7.263 | 60.5 | 99.2:0.8 | 6.81 |
| C | 3.823 | 3.880 | 11.685 | 7.399 | 59.2 | 98.6:1.4 | 6.82 |

The FESEM of the sample surface images for annealed samples A and B and non-annealed sample C are shown in Figure 2. The images revealed that all the samples exhibited randomly distributed grains in various orientations. The annealing process has no obvious impact on the microstructure except for the existence of some pores, which appeared to be less for the samples annealed at 650 °C and 500 °C for 12 h under $O_2$ flow compared with sample C was only sintered at 980 °C under $O_2$ flow with no annealing. The grain size was determined from 100 randomly chosen grains by using ImageJ software. The average grain sizes for the samples were 1.59, 1.51 and 1.23 μm for sets A, B and C, respectively. Notably, the annealing led to a slight increase in the grain size. Nevertheless, sample A exhibited a higher degree of grain compactness and the best homogeneous structure, resulting in improved inter-grain linkage and enhanced grain connectivity. In the context of the quantitative investigation, it was confirmed through EDX spectra that the $YBa_2Cu_3O_{7-\delta}$ phase was successfully formed and that the elements Y, Ba, and Cu existed in a ratio of 1:2:3 for all samples.

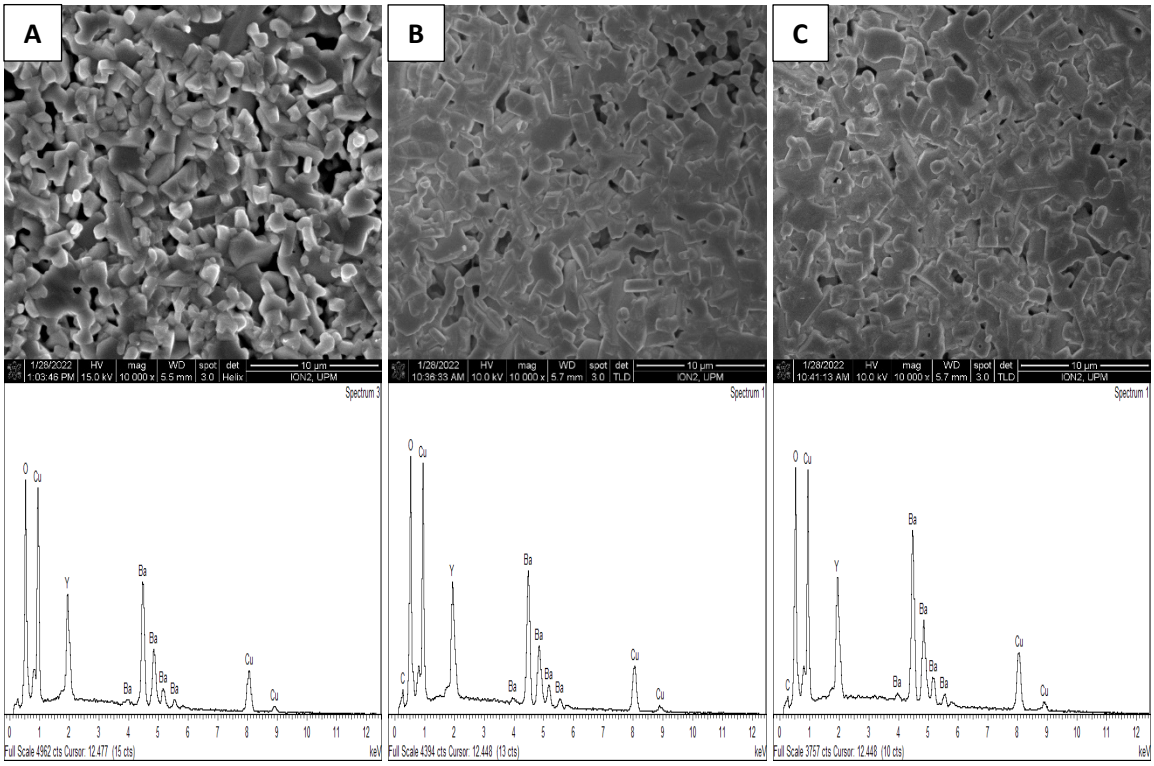

Figure 2. FESEM micrographs along with the EDX spectrum of the $YBa_2Cu_3O_{7-\delta}$ samples: (A) annealed at 650 °C, (B) annealed at 500 °C and (C) without annealing

Figure 3 shows the resistivity versus temperature curves ($\rho$-$T$) for samples A, B and C of bulk $YBa_2Cu_3O_{7-\delta}$. The normal state resistivity temperature curves exhibited metallic behaviour for all samples, followed by a sharp single transition to the superconducting state. The onset and zero transition temperatures, $T_{c\text{-onset}}$ and $T_{c\text{-zero}}$ were estimated by plotting the temperature derivative of the resistivity ($d\rho/dT$) as shown in Figure 4. The $T_{c\text{-onset}}$ and $T_{c\text{-zero}}$ of 95.6 K and 91.7 K were achieved for sample A, which was annealed at 650 °C, while the sample sintered without annealing exhibited the lowest $T_{c\text{-onset}}$ and $T_{c\text{-zero}}$. The present study has achieved the highest $T_{c\text{-onset}}$ compared to the values obtained from other studies for the pure $YBa_2Cu_3O_{7-\delta}$ sample prepared through the thermal treatment method [15,16,19,27,28]. Another obvious insight that should also be addressed is that the residual resistivity, $\rho_0$, was the lowest for sample A. This reduction is evident in the weak-link improvement between the grains as a result of the annealing at 650 °C. Furthermore, the observed reduction in resistivity could potentially be attributed to an enhancement in inhomogeneity, a decrease in the number of pores, disorders, and defects within the specimen samples [29–31]. The width of the superconducting transition, $\Delta T_c$, was observed to decrease as the samples were subjected to higher annealing temperatures. Conversely, the sample that was not annealed exhibited a broader superconducting transition width. Thus, sample A displayed a single and sharp peak compared with samples B and C. Table 4 summarises the data for $T_{c\text{-onset}}$, $T_{c\text{-zero}}$, $\Delta T_c$ and residual resistivity, $\rho_0$.

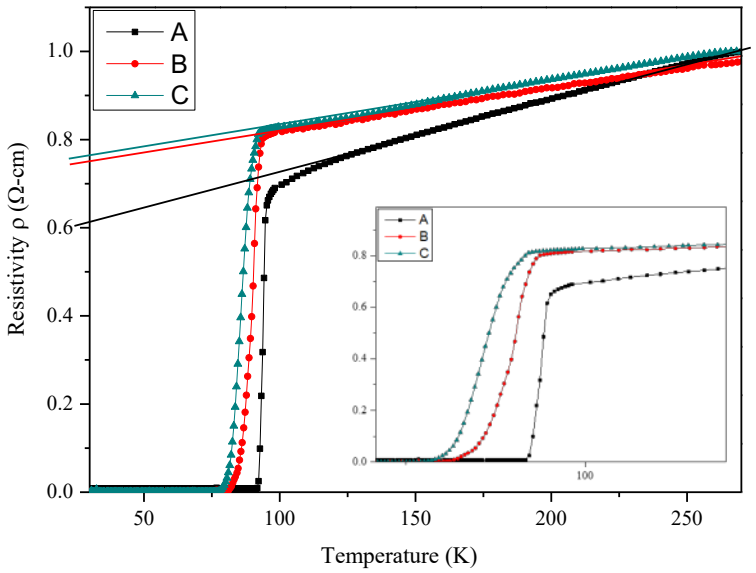


Figure 3. Resistivity versus temperature curves for $YBa_2Cu_3O_{7-\delta}$ samples: (A) annealed at 650 °C, (B) annealed at 500 °C and (C) without annealing

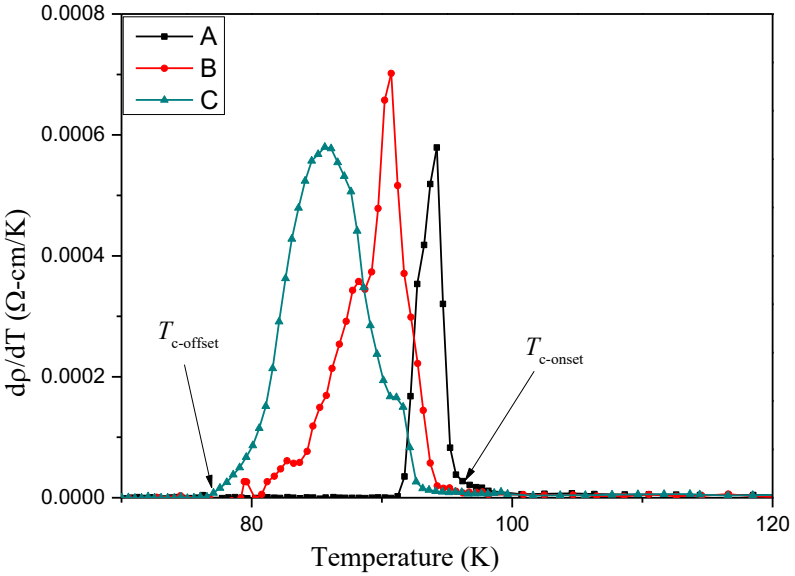


Figure 4. The derivative of resistivity against temperature for $YBa_2Cu_3O_{7-\delta}$ samples: (A) annealed at 650 °C, (B) annealed at 500 °C and (C) without annealing

Table 2. $T_{c\text{-onset}}$, $T_{c\text{-zero}}$, $\Delta T_c$ and $\rho_0$ of $YBa_2Cu_3O_{7-\delta}$ A, B and C samples

| Samples | $T_{c\text{-onset}}$ (K) | $T_{c\text{-zero}}$ (K) | $\Delta T_c$ (K) | $\rho_0$ (Ω.cm) |
|---|---|---|---|---|
| A | 95.6 | 91.7 | 3.9 | 0.61 |
| B | 93.7 | 83.6 | 10.1 | 0.74 |
| C | 92.6 | 78.0 | 14.6 | 0.76 |

## CONCLUSIONS

Thermal treatment was successfully used to prepare $YBa_2Cu_3O_{7-\delta}$ superconductors. The study involved exposing the samples to various annealing at temperatures of 650 °C and 500 °C (sets A and B), in addition to the samples that were not subjected to annealing (set C). The formation of the orthorhombic $YBa_2Cu_3O_{7-\delta}$ phase was successfully confirmed through XRD and EDX analyses. The results revealed that the annealed powder for set A was predominant in the single phase $YBa_2Cu_3O_{7-\delta}$, with the $Y_2BaCuO_{5-\delta}$ (Y211) phase observed for sets B and C. All samples showed metallic behaviour at normal state while their resistivity reduced with increasing annealing temperature. The annealing procedure at 650 °C yields the highest $T_{c\text{-onset}}$, with the sharpest transition, $\Delta T_c$, for sample A.


## ACKNOWLEDGEMENTS

This research is funded by the Ministry of Higher Education (MOHE) under FRGS Grant No. FRGS/1/2017/STG02/UPM/02/4 and IPS Grant No. 9666600 Universiti Putra Malaysia.


## REFERENCES


[1] M.K. Wu, J.R. Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Y.Q. Wang and C.W. Chu (1987), *Physical Review Letters* **58**(9), 908.

[2] X.P. Jiang, J.S. Zhang, J. G. Huang, M. Jiang, G.W. Qiao, Z.Q. Hu and C.X. Shi (1988), *Materials Letters* **7**(7-8), 250.

[3] G.R. Paz-Pujalt, A.K. Mehrotra, S.A. Ferranti and J.A. Agostinelli (1989), *Solid State Ionics* **32**, 1179.

[4] K. Schwarz (1990), *Microchimica Acta* **101**, 149.

[5] A. Bhargava, I. D. Mackinnon, T. Yamashita and D. Page (1995), *Physica C: Superconductivity* **241**(1-2), 53.

[6] A. Manthiram and J. B. Goodenough (1987), *Nature* **329**, 701.

[7] P. Peshev, G. Gyurov, I. Khristova, K. Petrov, D. Kovacheva, Ya. Dimitriev, N. Nencheva, E. Vlakhov (1988), *Materials Research Bulletin* **23**, 1765.

[8] M.K. Van Bael, A. Kareiva, G. Vanhoyland, J. D'Haen, M. D'Olieslaeger, D. Franco, C. Quaeyhaegens, J. Yperman, J. Mullens and L.C. Van Poucke (1998), *Physica C: Superconductivity* **307**, 209.

[9] J. Yuh, L. Perez, W.M. Sigmund and J.C. Nino (2007), *Journal of Sol-Gel Science and Technology* **42**(3), 323.

[10] J.G. Fagan and V.R.W. Amarakoon (1992), *AIP Conference Proceedings* **273**, 378.

[11] M.M. Dihom, A.H. Shaari, H. Baqiah, N.M. Al-Hada, S.K. Chen, R.B.A.S. Azis, M.M.A. Kechik and R. Abd-Shukor (2017), *Solid State Phenomena* **268**, 325.

[12] M.G. Naseri, E.B. Saion, H.A. Ahangar, M. Hashim and A.H. Shaari (2011), *Powder Technology* **212**(1), 80.

[13] M. Goodarz Naseri, E.B. Saion, H. Abbastabar Ahangar, A.H. Shaari and M. Hashim (2010), *Journal of Nanomaterials* Article ID 907686.

[14] M.G. Naseri, E.B. Saion, M. Hashim, A.H. Shaari and H.A. Ahangar (2011), *Solid State Communications* **151**(14-15), 1031.

[15] M.M. Dihom, A.H. Shaari, H. Baqiah, N.M. Al-Hada, S.K. Chen, R.B.A.S. Azis, M.M.A. Kechik, Z.A. Talib and R. Abd-Shukor (2017), *Results in Physics* **7**, 407.

[16] A.N. Kamarudin, M.M.A. Kechik, S.N. Abdullah, H. Baqiah, S.K. Chen, M.K.A. Karim, A. Ramli, K.P. Lim, A.H. Shaari, M. Miryala, M. Murakami, M. and Z.A. Talib (2022), *Coatings* **12**(1), 1.
[17] N.A.C. Dzul-Kifli, M.M.A. Kechik, S.H.M.N. Azam, H. Baqiah, A.H. Shaari, K.P. Lim, S.K. Chen, N.N.M. Yusuf, S.I.A. Sukor and M. Miryala (2021), *Solid State Science and Technology* **29**(1), 32.
[18] N.N. Yusuf (2018), Influence of $NbO_2$ and $SnO_2$ Additions on the Properties of $YBa_2Cu_3O_{7-d}$ Bulk Superconductor Synthesised Via Thermal Treatment Method, MSc. Thesis, Universiti Putra Malaysia
[19] N.A.C. Dzul-Kifli, M.M.A. Kechik, H. Baqiah, A.H. Shaari, K.P. Lim, S.K. Chen, S.I.A. Sukor, M.K. Shabdin, M. K.A. Karim, K.K.M. Shariff and M. Miryala (2022), *Nanomaterials* **12**(22), 3958.
[20] Y. Ito, H. Hasegawa, K. Takagi and K. Miyauchi (1987), *Japanese Journal of Applied Physics* **26**(5A), L692.
[21] P. Monod, M. Ribault, F. D'yvoire, J. Jegoudez, G. Collin and A. Revcolevschi (1987), *Journal de Physique* **48**(8), 1369.
[22] A. K. Tyagi, S. Tyagi and T.P. Sharma (1997), *Materials Science and Engineering: B* **45**(1-3) 88.
[23] H.S. Kim, J.B. Song, N.Y. Kwon, K.L. Kim and H.G. Lee (2009), *Superconductor Science and Technology* **22**(12), 125016.
[24] P. Benzi, E. Bottizzo and N. Rizzi (2004), *Journal of Crystal Growth* **269**(2–4), 625.
[25] K. Grigorov, V. Tsaneva, A. Spasov, W. Matz, R. Groetzschel and H. Reuther (2002), *Vacuum* **69**(1-3), 315.
[26] A.L. Patterson (1939), *Physical Review* **56**(10), 978.
[27] N.N. Mohd Yusuf, M.M.A. Kechik, H. Baqiah, S. K. Chen, K.P. Lim, A.H. Shaari, W.N.W. Wan Jusoh, S.I. Abd Sukor, M. Mousa Dihom Z.A. Talib and R. Abd-Shukor (2018), *Materials* **12**(1), 92.
[28] S.H. Yap, M.M. Kechik, S.K. Chen, A.N. Kamarudin, H. Baqiah, K.P. Lim, M.K.A. Karim, S.A. Halim, A. Doyan and K.K. Shariff (2023), *AIP Conference Proceedings* **2619**(1), 020003
[29] Y. Slimani, E. Hannachi, A. Hamrita, M.K. Ben Salem, F.B. Ben Azzouz, A. Manikandan and M. Ben Salem (2018), *Ceramics International* **44**(16), 19950.
[30] Y. Slimani, M.A. Almessiere, E. Hannachi, M. Mumtaz, A. Manikandan, A. Baykal, and F.B. Ben Azzouz (2019), *Ceramics International*, *45*(6), 6828–6835.
[31] Y. Slimani, M.A. Almessiere, E. Hannachi, F.O. Al-qwairi, A. Manikandan, A. Baykal, and F.B. Ben Azzouz (2019), *Ceramics International* **45**(17), 21864.