Effect of Preparation and Annealing Temperature on the Properties of (Hg,Tl)-2223 Superconductor

Ali Alnakhlani,1* Belqees Hassan,1 M. A. Ahlam1 and Muhammad Abdulhafiz2

1Faculty of Sciences, Department of Physics, Ibb University, 70270 Ibb, Yemen
2Faculty of Sciences, Department of Physics, Damascus University, 36822 Syria

*Corresponding author: ali5_2003@yahoo.com

Published online: 25 April 2019

To cite this article: Alnakhlani, A. et al. (2019). Effect of preparation and annealing temperature on the properties of (Hg,Tl)-2223 superconductor. J. Phys. Sci., 30(1), 71–79, https://doi.org/10.21315/jps2019.30.1.6

To link to this article: https://doi.org/10.21315/jps2019.30.1.6

ABSTRACT: Samples of superconducting compounds were prepared by a solid-state reaction technique in a sealed quartz tube under normal pressure. The impact of the compound on the electrical properties has been studied using the electrical resistance measurements of the samples as a function of temperature. The obtained results appear that an enhancement in the phase formation, and the superconducting transition temperature \( T_c \) were improved. It may be due to the decreasing of the magnetic impurities or the delocalisation of carriers which resulted in the enhancement of the density of mobile carriers in the conducting CuO\(_2\) planes.

Keywords: Superconducting, annealing, temperature resistance zero, mobile carriers

1. INTRODUCTION

Most studies on high-temperature superconductivity (HTS) have been concentrated on reaching the highest superconducting transition temperature, \( T_c \). The homologous series of \( \text{HgBa}_2\text{Ca}\(_{n-1}\)\text{Cu}_n\text{O}_{2n+2+\delta} \) [Hg-I2(n-1)n] consists of two types of layers, i.e., charge reservoir layers (CRL) \( \text{HgBa}_2\text{O}_\delta \) and infinite layers (IL) \( \text{Ca}\(_{n-1}\)\text{Cu}_n\text{O}_{2n} \), where \( n \) is the number of CuO\(_2\) planes that exist between two CRLs and supply holes to the above-mentioned CuO\(_2\) planes.\(^1\) Concentration of charge carrier in the CuO\(_2\) planes plays an important role in high \( T_c \) superconductors.

\( T_c \) of \( \text{HgBa}_2\text{Ca}\(_{n-1}\)\text{Cu}_n\text{O}_{2n+2+\delta} \) phases strongly depend on two parameters: oxygen content (\( \delta \)) and number (\( n \)) of (CuO\(_2\)) planes in their structures.\(^2,3\) The number of CuO\(_2\) planes (\( n \)) dependence of \( T_c \) is an interesting problem that may bring

© Penerbit Universiti Sains Malaysia, 2019. This work is licensed under the terms of the Creative Commons Attribution (CC BY) (http://creativecommons.org/licenses/by/4.0/).
important information to understand the high-$T_c$ superconductivity. Figure 1 shows the dependence of $T_c$ versus $n$. In this family of materials, the transition temperature sequentially increases with increasing number $n$ of CuO$_2$ planes up to $n = 3$, and then it is observed to decrease with further increase of $n$. Each phase has a different transition temperature to the superconducting state: for $n = 1$ (1201), $T_C = 97$ K; $n = 2$ (1212), $T_C = 127$ K; $n = 3$ (1223), $T_C = 135$ K; $n = 4$ (1224), $T_C = 126$ K; $n = 5$ (1245), $T_C = 110$ K; and $n = 6$ (1256), $T_C = 107$ K.

![Figure 1: Variation of $T_c$ as a function of $n$ for HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+\delta}$](image)

Previous studies on high $T_c$ superconductor have shown that the chemical doping or substitution, preparation conditions and hole concentrations play very important roles in high $T_c$ and conventional superconductors.\textsuperscript{4,5} To improve critical transition temperature of the (Hg,Tl)-2223 compound, samples were prepared with different conditions of annealing at different temperatures. It is very important to investigate impact of varying annealing conditions on the oxygen content of the (Hg,Tl)-2223 samples. Decreasing oxygen content in the sample leads to increase in $T_c$. However, if the oxygen content increases, this allows for forming of other phases inside the sample due to the increase of the pressure inside the quartz tube.\textsuperscript{6} Thus, it is useful to observe the variation of both the superconducting properties, as well as the normal state properties of materials as a function of changing preparation, annealing temperature and time annealing in order to understand superconductivity better.
Therefore, the aim of the current study is to synthesise and characterise the (Hg,Tl)-2223 high temperature superconductor and to investigate the effects of the preparation, annealing temperature and time annealing on the properties of these superconducting samples. The results of the present study may provide useful information to further studies of the properties of (Hg,Tl)-2223 superconductors and the optimisation of the annealing processes for (Hg,Tl)-2223 superconductors.

2. EXPERIMENTAL

Samples with the nominal composition of (Hg_{0.1},Tl_{0.9})_2Ba_2Ca_2Cu_3O_{8+δ} were prepared by the standard solid-state reaction method in only one step. High purity (99.95%) chemicals of HgO, Tl_2O_3, BaO_2, CaO and CuO were used as starting materials. These oxides were mixed using an agate mortar to make fine powder which was sieved in 64 μm sieve to obtain a homogeneous mixture. The powder was pressed in discs (1.5 cm in diameter and about 0.3 cm in thickness). Then, these discs were wrapped in a silver foil with 0.1 mm in thickness, which were put in sealed quartz tubes with a diameter of 1.5 cm and length of 15 cm. Next, the sealed tubes were put in closed stainless steel tubes, and the stainless steel tubes were placed horizontally in a furnace. Next, they were heated at a rate of 4°C min⁻¹ to (700°C/811°C). The samples have been maintained at this temperature for 6 h, and then they were cooled to room temperature at a rate of 0.5°C min⁻¹. (Hg,Tl)-2223 superconducting samples were annealed in normal atmosphere at 500°C for different time.

A closed cryogenic refrigeration system was used to perform the measurements of DC resistance for all samples with the four-probe method. The four contacts on the samples were made by a conductive silver paint. During resistance measurements a constant current of 2 mA has run through the sample, which was provided from a Keithley 2400 current source to avoid heating effects on the samples.

3. RESULTS AND DISCUSSION

Figure 2 shows behaviour of normalised resistance R (T)/R (300K) versus temperature for (Hg,Tl)-2223 samples before and after annealing. It is clear that the annealed sample has a tail and its resistance zero at a temperature of 79 K. This may be due to missing oxygen content. Figure 1 shows that the annealing has improved the phase transition and the semiconducting-like behaviour in the normal state was absent for the sample S₁. The onset temperature (T_{c,onset}) was increased from 111 K to 117 K. A value of zero electrical resistance (T_{c,offset}) was 63 K before annealing, and became as 79 K after annealing, being higher by the annealing process.
There are two possibilities for enhancing $T_c$ in the (Hg,Tl)-2223 samples annealed under normal condition. First is by increasing the amount of oxygen in the bulk to increase the concentration of holes in $p-d_{x^2-y^2}$ bounded. Second is possibility to reduce the amount of extra oxygen from the sample to decrease the undesired phases (magnetic, non-superconductor). It was previously reported that $T_c$ of T1-2223 samples synthesised under ambient pressure was substantially enhanced by the annealing in an evacuated tube.\textsuperscript{7}

Figure 2 shows the results of resistance measurements for the as-sintered samples sintered at 700°C (sample S\textsubscript{1}) and 811°C (sample S\textsubscript{2}) for 6 h. Clearly, it is noticeable that the sample S\textsubscript{1} has two phases, but with the sample S\textsubscript{2}, it is almost single phase. This means that the second phase has disappeared when the sample sintered at 811°C. It is important to mention that the S\textsubscript{2} sample was improved in connectivity and the improvement is related to the uniform distribution and alignment of superconducting grains. Also, as shown in Figure 3, the resistance decreases with temperature from 300 K like a metal for the S\textsubscript{2} sample, whereas the S\textsubscript{1} sample does not. The results of $R (T)$ show that the sample has semiconducting-like behaviour in the normal state. This may be due to the reduced oxygen concentration in the bulk that may act as effective channelling centres of oxygen vacancies.\textsuperscript{8,9} The values of $T_c^{onset}$ and $T_c^{offset}$, which are determined from the electrical resistance behaviour are
111 K and 63 K respectively for S₁ sample, while the \( T_c^{\text{onset}} \) and \( T_c^{\text{offset}} \) for the S₂ sample are 107 K and 93 K, respectively. The transition width \( \Delta T_c = T_c^{\text{onset}} - T_c^{\text{offset}} \) determined from the difference between the onset temperature and zero resistance temperature for (Hg,Tl)-2223 samples are listed in Table 1.

| Temperature (K) | R(T)/R(300K) |
|----------------|---------------|
| 300            | 200           |
| 100            | 150           |
| 50             | 0.5           |
| 0.2            | 0.4           |
| 0.6            | 0.8           |
| 1.0            | S₂ (811 °C)   |
|                | S₁ (700 °C)   |

Figure 3: Temperature dependence of the normalised resistance for (Hg,Tl)-2223 sample sintered at 700°C and at 811°C for 6 h.

Figure 4 shows the temperature dependence of a normalised resistance for S₂ samples at different annealing time at 0 T. It is observed that all samples (above the transition temperature onset \( T_c^{\text{onset}} \)) have a linear metallic behaviour in the normal state. By decreasing the annealing time, the metallicities increases. More metallic behaviour may be attributed to the best grain connection or to optimal carrier doping in the CuO₂ conducting planes of the sample under high oxygen pressure.\(^1⁰\) \( T_c^{\text{onset}} \), determined from the electrical resistance behaviour when the resistance first drops, is equal to 107 K for S₂ sample. When the sample was annealed at 500°C for 4 h (sample S₂₁), \( T_c \) increased by about 7 K to 114 K. Further annealing at 500°C for 2 h (sample S₂₂) enhanced \( T_c \) up to 122 K. It is clear that the transition width decreased with decreasing annealing time, and the annealing improved the coupling characteristics between superconducting grains. The different values for all samples determined from the resistance measurements are listed in Table 1.

Annealing the samples in normal conditions leads to a decrease of resistance and to an increase of \( T_c \), in agreement with the results of other studies.\(^1¹⁻¹⁹\)
Properties of (Hg,Tl)-2223 Superconductor

Figure 4: Normalised resistance vs. temperature measurements of S₂ sample annealed at 500°C for 4 h and 2 h.

Table 1: Sample preparation with heat treatment conditions, normal-state resistance (R₃₀₀), residual resistance (R₀), T_c^{offset}, T_c^{onset}, and ΔT_c from resistance measurement.

| Samples | Annealing time (h) | R₃₀₀ (Ω) | R₀ (Ω) | T_c^{onset} (K) | T_c^{offset} (K) | ΔT_c (K) |
|---------|-------------------|----------|--------|-----------------|-----------------|----------|
| S₁      | 0                 | 1.7052   | 2.22875| 111             | 63              | 48       |
| S₁₂     | 4                 | –        | 3.00446| 117             | 79              | 38       |
| S₂      | 0                 | 0.0712   | 0.06031| 107             | 93              | 14       |
| S₂₁     | 4                 | 0.0378   | 0.00910| 114             | 103             | 11       |
| S₂₂     | 2                 | 0.0323   | 0.00458| 122             | 112             | 10       |

The normal-state resistance (R₃₀₀) and residual resistance (R₀) as a function of annealing time are plotted in Figure 4 for (Hg,Tl)-2223 sample before and after annealing. Here, R₃₀₀ is the resistance at 300 K and R₀ is obtained from the fitting of resistance data in the temperature range 2T_c K ≤ T ≤ 300 K, according to Matthiessen’s rule.²⁰

It can be observed from Figure 5 that the sample S₂ has highest room temperature resistance R₃₀₀ (0.0712 Ω) while the sample S₂₂ has lowest R₃₀₀ (0.0323 Ω). The post annealing at 500°C and 811°C (S₂₂) enhances the value of resistance at 300 K. One of the possible contributions to the room temperature resistance is
from the defects present in the samples. The defects may be due to the presence of impurities and weak links between the superconducting grains. During annealing, the oxygen content and thus the density of mobile carriers of the superconducting phase could increase, giving rise to a decrease in resistance. After annealing in normal conditions, the S22 sample had a critical temperature $T_{c,\text{onset}} = 122$ K with a transition width $\Delta T_c = 10$ K. It may be due to the decreasing of the magnetic impurities or the delocalisation of carriers which results in the increase of the holes concentration in the conducting CuO$_2$ planes.

![Figure 5: The $R_{300}$ and the $R_0$ as a function of annealing time for (Hg,Tl)-2223 sample.](image)

**4. CONCLUSION**

The current study has investigated the influence of preparation, annealing temperature and time annealing on the properties of the (Hg,Tl)-2223 superconductor ($T_{c,\text{onset}}$ and $T_{c,\text{offset}}$). The results of R (T) measurements have shown that the optimised annealing temperature is 811°C for 2 h. The highest $T_c$ of S22 sample in this study was $T_{c,\text{onset}} = 122$ K and at $T_{c,\text{offset}} = 112$ K. The increased pressure inside the quartz tube allows the formation of other phases inside the sample when the samples were annealing in air (normal conditions). The inter-grain superconductivity in (Hg,Tl)-2223 samples may be significantly affected by the time and the annealing temperature.
5. ACKNOWLEDGEMENTS

The authors would like to thank the anonymous reviewers for their valuable comments and suggestions to improve the quality of the paper. This work was supported by Ibb University, Yemen and Damascus University, Syria.

6. REFERENCES

1. Shivagan, D. et al. (2008). AC-susceptibility study on vortex-molecule lattice in supermultilayer cuprate \( \text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta} \) \((n = 14)\). \textit{Phys. C}, 468(15), 1281–1286, https://doi.org/10.1016/j.physc.2008.05.213.

2. Antipov, E. V., Abakumov, A. M. & Putilin, S. N. (2002). Chemistry and structure of Hg-based superconducting Cu mixed oxides. \textit{Supercond. Sci. Technol.}, 15(7), R31, https://doi.org/10.1088/0953-2048/15/7/201.

3. Iyo, A. et al. (2006). Synthesis and physical properties of multilayered cuprates. \textit{Phys. C Supercond. App.}, 445, 17–22, https://doi.org/10.1016/j.physc.2006.03.067.

4. Liang, B. et al. (2002). Effect of vacuum annealing on the structure and superconductivity of \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8+\delta \) single crystals. \textit{Phys. C Supercond.}, 366(4), 254–262, https://doi.org/10.1016/S0921-4534(01)00910-8.

5. Terzioglu, C., Varilci, A. & Belenli, I. (2009). Investigation of effect of annealing temperature on mechanical properties of \( \text{MgB}_2 \). \textit{J. Alloys Comp.}, 478(1–2), 836–841, https://doi.org/10.1016/j.jallcom.2008.12.044.

6. Ali Yusuf, A. et al. (2011). Effect of \( \text{Ge}^{4+} \) and \( \text{Mg}^{2+} \) doping on superconductivity, fluctuation induced conductivity and interplanar coupling of \( \text{TlS}_2\text{CaCu}_2\text{O}_{7+\delta} \) superconductors. \textit{Phys. C Supercond.}, 471, 363–372, https://doi.org/10.1016/j.physc.2011.03.007.

7. Tatsuki, T. et al. (1997). Annealing study on \( \text{Hg, Tl}_{2}\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta} \) \((n=1–5)\) superconductors. \textit{Phys. C Supercond.}, 278(3–4), 160-168, https://doi.org/10.1016/S0921-4534(97)00117-2.

8. Martynova, O. A. & Gasumyants, V. E. (2008). On the transformation of the normal-state band spectrum of \( \text{Tl-based HTSC’s} \) with increasing number of \( \text{CuO2} \) layers and doping level. \textit{Phys. C}, 468, 394–400, https://doi.org/10.1016/j.physc.2007.12.007.

9. Abbas, M. M., Abass, L. K. & Salman, U. (2012). Influences of sintering time on the \( T_C \) of \( \text{Bi}_{2.4}\text{Cu}_{0.7}\text{Pb}_{0.3}\text{Sr}_{2}\text{Ca}_3\text{Cu}_4\text{O}_{10+\delta} \) high temperature superconductors. \textit{Energy Proced.}, 18, 215–224, https://doi.org/10.1016/j.egypro.2012.05.033.

10. Gao, L. et al. (1993). Study of superconductivity in the \( \text{Hg-Ba-Ca-Cu-O} \) system. \textit{Phys. C Supercond.}, 213(3–4), 261–265, https://doi.org/10.1016/0921-4534(93)90440-2.

11. Khan, N. A., Husain, G. & Sabeeh, K. (2006). Enhanced superconductivity in \( \text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_{2}\text{Ca}_{n-1-y}\text{Be}_y\text{Cu}_n\text{O}_{2n+4-\delta} \) \((n= 3, 4 \text{ and } y = 0.7, 1.5, 1.7, 2.0) \) system with oxygen doping. \textit{J. Phys. Chem. Solids}, 67(8), 1841–1849, https://doi.org/10.1016/j.jpcs.2006.04.010.
12. Carrasco, M. F. et al. (2006). Annealing time effect on Bi-2223 phase development in LFZ and EALFZ grown superconducting fibres. Appl. Surf. Sci., 252(14), 4957–4963, https://doi.org/10.1016/j.apsusc.2005.07.025.
13. Hirai, M. et al. (2007). Annealing effect on Tc in the multi-layered cuprate superconductor (Cu,C)Ba2CaCu2Oy. Phys. C Supercond. App., 460–462, 450–451, https://doi.org/10.1016/j.physc.2007.03.183.
14. Irfan, M. & Khan, N. A. (2010). Study of phonon modes and superconducting properties of the oxygen post-annealed (Cu0.5Tl0.5) Ba2CaCu2−yGeyO2n+4−δ (n=3, 4 and y=0, 0.5, 0.75, 1.0) superconductors. Cryogen., 50(2), 61–65, https://doi.org/10.1016/j.cryogenics.2009.11.001.
15. Wang, X. G., Huang, Z. & Yuan, L. (1995). Effect of F-doping in the Hg-Ba-Ca-Cu-O system. Phys. C Supercond., 253(3–4), 254–258, https://doi.org/10.1016/0921-4534(95)00527-7.
16. Shao, H. M. et al. (1997). Optimization and enhancement of transition temperature for HgBa2Ca2Cu3O8+δ ceramic superconductors. Phys. C Supercond., 282–287, 1559–1560, https://doi.org/10.1016/S0921-4534(97)00925-8.
17. Ha, D. H. et al. (2000). Effects of Sr substitution on Tc of Y0.85Ca0.15Ba2−xSrxCu3Oy. Phys. C Supercond., 341–348, 607–608, https://doi.org/10.1016/S0921-4534(00)00611-0.
18. Shen, Z. et al. (2013). Electrospinning preparation and high-temperature superconductivity of YBa2Cu3O7−x nanotubes. J. Mater. Sci., 48(11), 3985–3990, https://doi.org/10.1007/s10853-013-7207-y.
19. Kajitani, J. et al. (2014). Correlation between crystal structure and superconductivity in LaO0.5F0.5BiS2. Solid State Commun., 181, 1–4, https://doi.org/10.1016/j.ssc.2013.11.027.
20. Awad, R. et al. (2008). Superconducting properties of zinc substitution in Tl-2223 phase. J. Alloys Comp., 460(1–2), 500–506, https://doi.org/10.1016/j.jallcom.2007.05.100.
21. Khurram, A. A. et al. (2011). Effect of ion irradiation induced defects on the excess conductivity of Cu1−xTlBa2CaCu2O4−δ superconductor thin films. Phys. C Supercond., 471(1–2), 35–41, https://doi.org/10.1016/j.physc.2010.10.007.
22. Aytug, T. et al. (1999). Effect of sodium doping on the oxygen distribution of Hg-1223 superconductors. Phys. C Supercond., 313(1–2), 121–126, https://doi.org/10.1016/S0921-4534(98)00699-6.