

Impact of SnF₂ Addition on AC Susceptibility and Electrical Properties of Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ Superconductor

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The effect of SnF₂ addition on the superconducting properties of Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ (SnF₂)_x with $x = 0-1.0$ wt. % is reported. All samples were prepared by the solid-state reaction route. The powder X-ray diffraction (XRD) patterns revealed a single Bi-2212 phase for all samples. Scanning electron micrographs showed plate-like structure which increased in grain sizes with SnF₂ addition. The temperature-dependent resistance measurement showed the highest $T_{c \text{ onset}}$ (91 K) was for $x = 0.5$ wt. % sample which belongs to the Bi-2212 phase. The susceptibility transition temperature, $T_{c\chi}$ for all samples was between 72-81 K. The lower peak temperature at the imaginary part of susceptibility χ'' , T_{p2} was suppressed with SnF₂ addition indicating the weakening of intergranular coupling and flux pinning force. This work showed that SnF₂ addition not only resulted in a single Bi-2212 phase but also enhanced the transition temperature and grains growth of Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈. The role of internal lattice strain in improving the transition temperature of Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ was also discussed.

Keywords: SnF₂; Bi-2212; internal lattice strain; AC susceptibility

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The Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈, also known as the Bi-2212 phase, is one of the interesting families of Bi-based cuprates superconductors. It superconducts at around 80 to 83 K [1, 2]. Although the critical temperature of Bi_{1.6}Pb_{0.4}Sr₂CaCu₂ (Bi-2223) is higher (118 K) [3] than the Bi-2212 phase superconductor, it is easier to form a single Bi-2212 phase than a Bi-2223 phase [4]. Moreover, the ability to sustain high field properties at low temperatures compared to other Bi-based families makes it advantageous for wire and tape applications [5-8]. However, the existing weak links between the grains and poor pinning capability pose significant drawbacks for this superconductor, which need to be overcome before it can be integrated into technological applications.

It is well known that adding elements and compounds to the Bi-based superconductor can enhance its superconducting properties. Additionally, introducing defects via radiation has been observed to increase the flux pinning capability of Bi-based superconductors [9, 10]. Recently, there has been an increased interest in exploring the influence of metal sulfides such as PbS [2], FeS [11], and Cr₂S₃ [12], CuS [13] on the Bi-based superconductor.

Apart from that, metal fluorides present another interesting avenue for potentially improving the cuprate-based high-temperature superconductor properties. It is also noteworthy that oxygen and fluorine share the same period (Period 2) in the periodic table. In the YBa₂Cu₃O₇ superconductor, the small amount of FeF₂ addition improved the transport and superconducting properties [14]. The transition temperature was enhanced for the nanosized NiF₂ added Bi-2223 superconductor [15]. NiF₂ added Bi-2223 tapes showed a significant improvement of J_c compared with the non-added tape [16].

The influence of various metal fluorides on Bi-2212 remains an interesting research area. In this study, we investigated the effect of SnF₂ addition on Bi-2212 superconductor. The SnF₂, also known as stannous fluoride, is an excellent ionic conductor due to the high polarizability of Sn²⁺ and weak coordination of F⁻ ion [17]. SnF₂ forms several solid electrolytes when combined with monovalent and divalent fluorides, making them highly appealing for diverse electrochemical applications and solid-state ionic devices [18, 19]. SnF₂ exhibits three polymorphic forms, with α -SnF₂ (monoclinic) stable

at room temperature. In the temperature range of 413–453 K, it transforms γ -SnF₂ (tetragonal), maintaining stability up to the melting temperature (488 K). Upon cooling, γ -SnF₂ undergoes a second-order phase transition to β -SnF₂ (orthorhombic) [20–22].

Hence, the interaction between SnF₂ and Bi-2212 is interesting to study. This work aimed to study the effects of SnF₂ addition on the superconducting properties of Bi-2212. The structure, microstructure, electrical properties, and AC Susceptibility were reported.

EXPERIMENTAL DETAILS

Powders with the starting formula of Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ were synthesized via the solid-state reaction method. High purity powders (99.9 %) of Bi₂O₃, PbO, SrCO₃, CaO, and CuO were weighed, ground, and heated to two consecutive 24 h heating cycle at 800 °C. The mixed black powder was subsequently ground and heated for 50 h at 840 °C. Then, SnF₂ powders were added with stoichiometry of Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ (SnF₂)_x with $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 1.0 wt. %. The resultant powders were formed into pellets with a diameter of 13 mm and a thickness of 2 mm. The pellets were heated at 840 °C for 24 h.

A Bruker D8 Advance X-ray diffractometer, utilizing Cu K α radiation, was employed to identify the phases. The lattice parameters were determined

using the Pawley method through Xpert' Highscore software. A JEOL Model JSM6010PLUS/LA scanning electron microscope (SEM) was employed to observe the microstructure of the samples.

The temperature-dependent DC electrical resistance measurements were carried out using the four-probe method with silver paint contacts, in conjunction with a CTI Cryogenics Model 22 closed-cycle refrigerator. A constant current source from a Lake Shore Model 340 ranging between 1 and 100 mA was used for all measurements.

For AC susceptibility measurements, an AC susceptometer from Cryo Industry with model number REF-1808-ACS was utilized. The samples were cut into bar shapes with a cross-section of 2 mm \times 2 mm, and an AC signal frequency of 295 Hz was applied with a constant magnetic field (5 Oe) parallel to the sample throughout the measurement.

RESULTS AND DISCUSSION

The powder X-ray diffraction pattern shown in Figure 1 revealed that a nearly single Bi-2212 (>97 %) phase was observed for all samples. This indicated that the SnF₂ did not suppress the Bi-2212 phase. Besides that, no peaks corresponding to SnF₂ were observed in all added samples. The Bi-2212 phase can be indexed based on the orthorhombic structure using ICDD database with number PDF-00-046-0781.

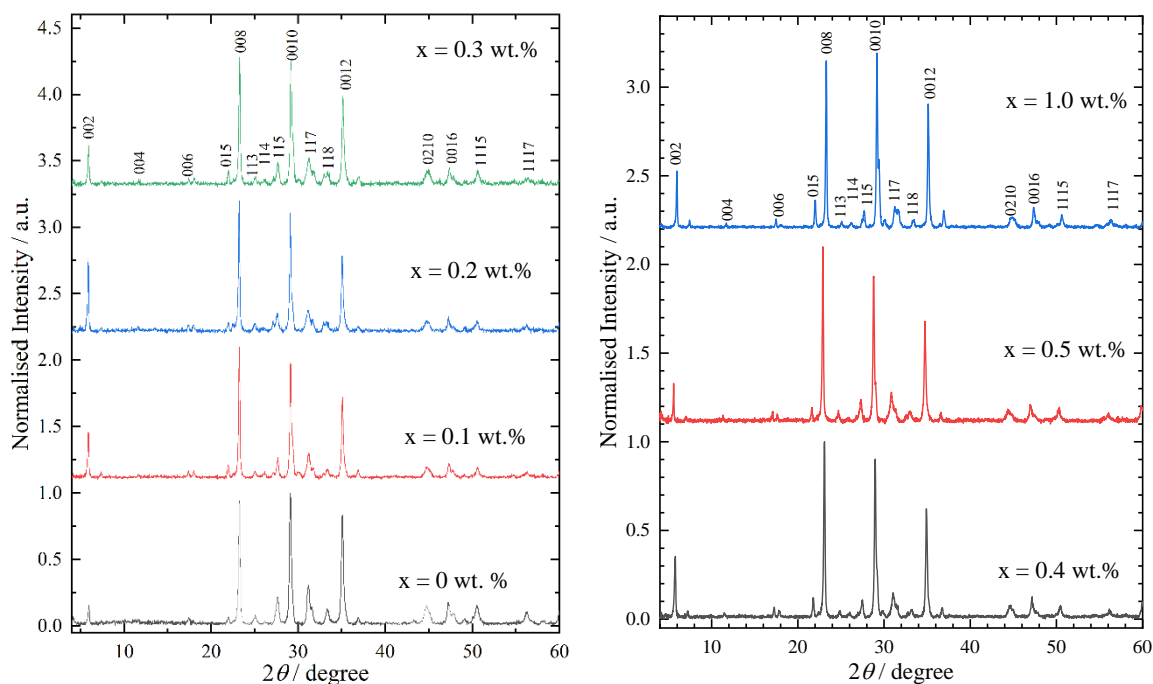


Figure 1. XRD pattern of Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ (SnF₂)_x with $x = 0$ –1.0 wt. %.

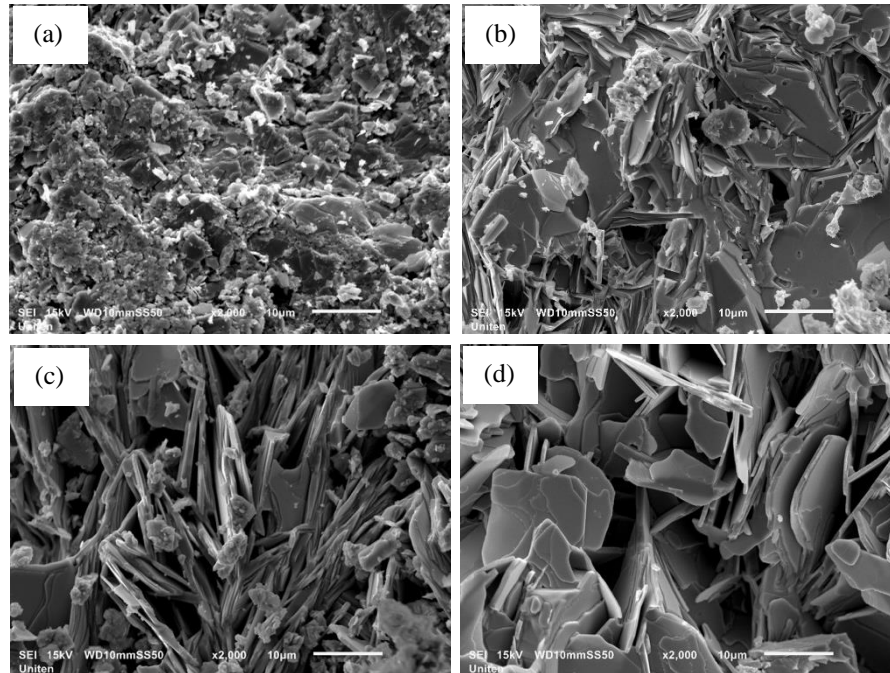


Figure 2. SEM micrograph of Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ (SnF₂)_x with (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.3$ and (d) $x = 0.5$ wt. %.

The lattice parameters for $x = 0$ wt. % sample were $a = 5.316 \text{ \AA}$, $b = 5.434 \text{ \AA}$ and $c = 30.705 \text{ \AA}$. All added samples showed an increase of lattice parameters a and c as well as unit cell volume compared to the non-added samples. This demonstrated that the Sn atom may be incorporated into the unit cell of the Bi-2212 phase. Nevertheless, additional direct measurements such as Rietveld refinement using neutron diffraction and XRD are essential to substantiate this claim. The internal lattice strain was calculated by the ratio c/a which is shown in Table 1. In general, the ratio c/a decreased for all added samples except for $x = 1.0$ wt. % sample. Typically, the elongation in c/a axes is connected to the lengthening of the Cu-O bond, which regulates the dimensions in major planes [23, 24]

Figures 2(a), 2(b), 2(c) and 2(d) show the SEM micrograph for $x = 0, 0.2, 0.3$ and 0.5 wt. % samples, respectively. All samples revealed a platelet-like and layered microstructure with some porosity. Partial melting was also observed for $x = 0, 0.2,$ and 0.3 wt. % samples. Besides that, the grain sizes increased as the amount of SnF₂ increased indicating that the SnF₂ promoted the grains growth of Bi-2212 phase.

The normalized electrical resistance versus temperatures curves for Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ (SnF₂)_x

with $x = 0-1.0$ wt. % are shown in Figure 3. In this work, $T_{c \text{ onset}}$ is the temperature at which the superconducting phase begins to occur, while $T_{c \text{ zero}}$ is the temperature at which the electrical resistance is zero. All samples exhibited normal metallic properties before onset transition temperature, $T_{c \text{ onset}}$ except for $x = 1.0$ wt. % sample. The $x = 1.0$ wt. % sample showed the semi-metal like behavior above $T_{c \text{ onset}}$. The $T_{c \text{ onset}}$ and zero transition temperature, $T_{c \text{ zero}}$ for $x = 0$ wt. % samples were 84 K and 71 K, respectively. In general, $T_{c \text{ onset}}$ was enhanced up until $x = 0.5$ wt. % but $T_{c \text{ zero}}$ was slightly suppressed after SnF₂ addition. The highest $T_{c \text{ onset}}$ was 91 K for the 0.5 wt. % sample. There was no systematic change in the transition width ΔT_c (11 -22 K) for all samples.

The improvement of $T_{c \text{ onset}}$ particularly with a low amount of addition can be ascribed to the increase in chemical pressure induced by the presence of Sn which was signified by the changes in internal lattice strains and the increase in unit cell volume [25]. Moreover, it was suggested that $T_{c \text{ onset}} = 91 \text{ K}$ for $x = 0.5$ % sample belonged to the Bi-2212 phase. This was supported by the XRD results, which indicated that no peaks belonging to the Bi-2223 phase were observed in any of the samples.

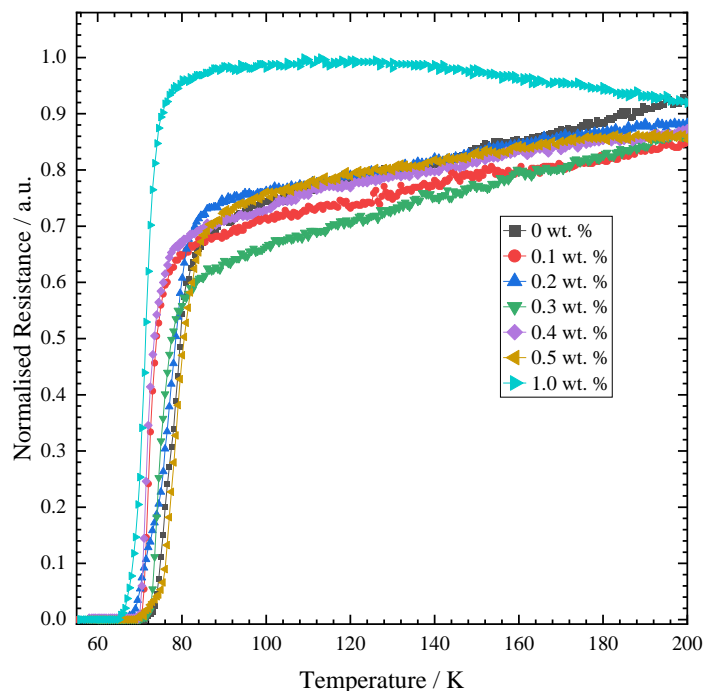


Figure 3. Normalized resistance versus temperature of Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ (SnF₂)_x with $x = 0-1.0$ wt. %.

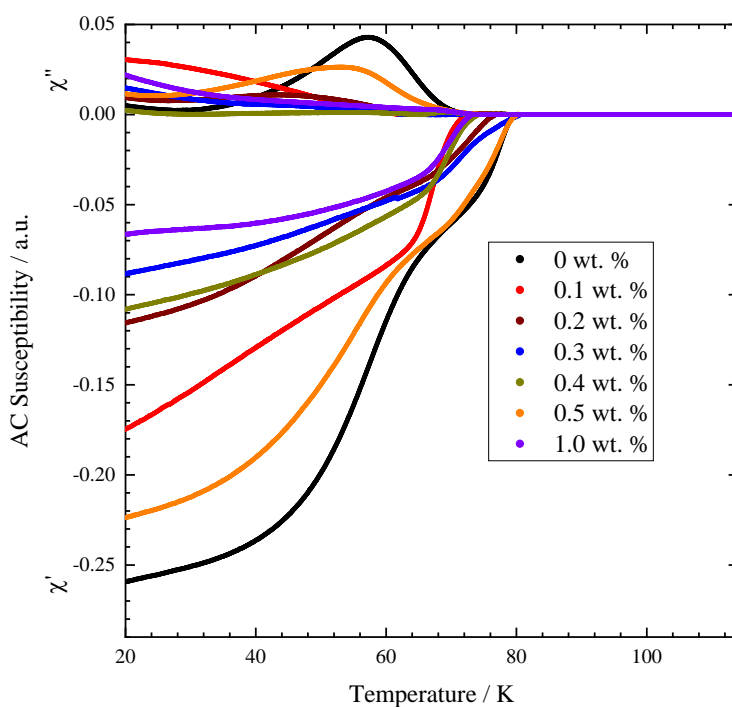


Figure 4. AC susceptibility of Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ (SnF₂)_x with $x = 0-1.0$ wt. %.

Figure 4 shows the AC susceptibility versus temperature of Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ (SnF₂)_x with $x = 0-1.0$ wt. %. The occurrence of diamagnetic shielding is denoted by the sudden drop in the real part, χ' of complex susceptibility ($\chi = \chi' + i\chi''$). This sudden drop is also known as susceptibility transition temperature,

$T_{c\chi'}$. $T_{c\chi'}$ for the non-added sample is 80 K. For added samples, $T_{c\chi'}$ was between 72 and 81 K.

In the imaginary part of susceptibility, two peaks representing AC losses should be observed in the samples. One small peak near the $T_{c\chi'}$ represents

the intrinsic loss and corresponds to intragranular properties, while a larger peak at lower temperatures denotes the intergranular behavior. In our work, the $x = 0, 0.1, 0.2, 0.4, 0.5$ and 1.0 wt. % samples (Figure 5) exhibited a peak corresponding to the intrinsic loss. The higher peak temperature, T_{p1} for $x = 0, 0.1, 0.2, 0.4, 0.5$ and 1.0 wt. % samples were 77, 67 K, 73 K, 70 K, 77 and 69 K, respectively. The lower peak temperature, T_{p2} is related to the intergranular couplings

and the strength of the flux pinning. If T_{p2} shifts to higher temperatures, it indicates an enhancement of intergranular coupling and flux pinning force [2]. T_{p2} for the non-added sample was 57 K. T_{p2} for all added samples were decreased (between 47 and 56 K) and further addition (1.0 wt. %) severely suppressed T_{p2} to the lower temperatures (< 20 K). This suggested that the addition of SnF₂ decreased the intergranular coupling and weakened the flux pinning force.

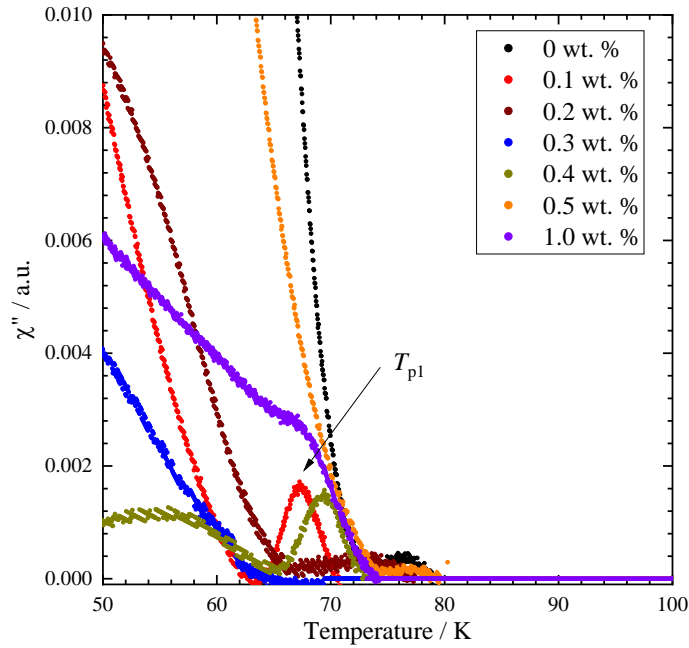


Figure 5. Imaginary part of susceptibility, χ'' of Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ (SnF₂)_x with $x = 0-1.0$ wt. %.

Table 1. $T_{c \text{ onset}}$, $T_{c \text{ zero}}$, ΔT_c , lattice parameter, V , c/a , $T_{c\chi'}$, T_{p1} and T_{p2} of Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ (SnF₂)_x with $x = 0-1.0$ wt. %.

Sample / wt. %	0	0.1	0.2	0.3	0.4	0.5	1.0
$T_{c \text{ onset}} / \text{K}$	84	80	88	87	80	91	79
$T_{c \text{ zero}} / \text{K}$	71	69	66	70	69	69	65
$\Delta T_c / \text{K}$	13	11	22	17	11	22	14
$a / \text{\AA}$	5.316	5.327	5.377	5.336	5.372	5.355	5.325
$b / \text{\AA}$	5.434	5.441	5.424	5.430	5.404	5.418	5.449
$c / \text{\AA}$	30.71	30.77	30.84	30.71	30.83	30.80	30.83
$V / \text{\AA}^3$	887.0	891.9	899.4	889.7	895.1	893.7	894.4
c/a	5.776	5.777	5.736	5.754	5.74	5.752	5.789
$T_{c\chi'} / \text{K}$	80	72	77	81	74	80	73
T_{p1} / K	77	67	73	-	70	77	69
T_{p2} / K	57	<20	47	50	56	54	<20

CONCLUSIONS

The effect of SnF₂ addition on Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ with $x = 0-1.0$ wt. % has been investigated. The Bi-2212 phase was not suppressed by SnF₂ addition. The grain growth was promoted with SnF₂ addition. The addition of a small amount of SnF₂ improved $T_{c\text{ onset}}$ of Bi-2212. The decrease in T_{p2} demonstrated that SnF₂ suppressed the intergrain coupling and flux pinning force. This work also showed that the changes in the internal lattice strains due to the SnF₂ play an important role in enhancing the transition temperature of Bi-2212 superconductor. Additional investigations involving other metal fluoride with different electrical and magnetic properties can be conducted to further explore their potential to enhance the performance of the Bi-2212 superconductor.

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REFERENCES

1. Tange, M., Amano, T., Nishizaki, S. and Yoshizaki, R. (2003) Superconducting properties of Bi-2212 whiskers. *Physica C: Superconductivity*, **392-396**, 428–431.
2. Masnita, M. J., Awang, R. and Abd-Shukor, R. (2022) AC susceptibility and electrical properties of PbS added Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ superconductor. *Sains Malaysiana*, **51(1)**, 315–328.
3. Wadia, K. M., Abdulateefa, A. N., Shabanb, A. H. and Jasimb, K. A. (2019) Improvement of superconducting properties of Bi₂Ba₂Ca₂Cu₃O_{10+δ} ceramic by prepared under different pressure. *Energy Procedia*, **157**, 222–227.
4. Tsukamoto, T., Triscone, G., Genoud, J. Y., Wang, K. Q., Janod, E., Junod, A. and Muller, J. (1994) Preparation and superconducting properties of high-quality Bi-2212 ceramics. *Journal of Alloys and Compounds*, **209(1)**, 225–229.
5. Marken, K. R., Dai, W., Cowey, L., Ting, S. and Hong, S. (1997) Progress in BSCCO-2212/silver composite tape conductors. *IEEE Transactions on Applied Superconductivity*, **7(2)**, 2211–2214.
6. Marken, K. R., Miao, H., Meinesz, M., Czabaj, B. and Hong, S. (2003) BSCCO-2212 conductor development at Oxford Superconducting Technology. *IEEE Transactions on Applied Superconductivity*, **13(2)**, 3335–3338.
7. Kametani, F., Jiang, J., Matras, M., Abramov, D., Hellstrom, E. E. and Larbalestier, D. C. (2015) Comparison of growth texture in round Bi2212 and flat Bi2223 wires and its relation to high critical current density development. *Scientific Reports*, **5(1)**, 8285.
8. Xin-Xin, Z., Xue, F., Gou, X. and Teng-Ming, S. (2019) Statistical study of the void structure of Bi2212 multifilamentary superconducting wires and its effect on the critical current density. *Engineering Computations*, **36(8)**, 2714–2725.
9. Hamid, N. A., Mohiju, Z. A. and Abdullah, Y. (2018) Effect of neutron irradiation on electrical properties of Bi₂Sr₂CaCu₂ (Bi-2212) phase superconductor. *Solid State Phenomena*, **280**, 21–25.
10. Ogikubo, K., Terai, T., Yamaguchi, K. and Yamawaki, M. (2000) Enhancement in critical current density of Bi-2212 single crystals by neutron irradiation followed by thermal annealing. *Physica C: Superconductivity*, **341-348**, 1469–1470.
11. Masnita, M. J. and Abd-Shukor, R. (2020) Iron sulfide effects on AC susceptibility and electrical properties of Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ superconductor. *Results in Physics*, **17**, 103177.
12. Farah-Elia, N. A. R., Ilhamsyah, A. B. P. and Abd-Shukor, R. (2019) Ferrimagnetic Cr₂S₃ effects on (Bi_{1.6}Pb_{0.4})Sr₂CaCu₂O₈ superconductor. *Journal of Materials Science: Materials in Electronics*, **30(13)**, 12031–12035.
13. Loudhaief, N., Ben Salem, M., Labiadh, H. and Zouaoui, M. (2020) Electrical properties and fluctuation induced conductivity studies of Bi-based superconductors added by CuS nanoparticles synthesized through the aqueous route. *Materials Chemistry and Physics*, **242**, 122464.
14. Wei, K., Kong, I. and Abd-Shukor, R. (2012) Superconducting and transport properties of FeF₂ added YBa₂Cu₃O₇ superconductor. *World Journal of Engineering*, 1–2.
15. Hafiz, M. and Abd-Shukor, R. (2014) Effects of nano-sized NiF₂ addition in Bi_{1.4}Pb_{0.6}Sr₂Ca₂Cu₃O_{10+δ} superconductor. *Advanced Materials Research*, **895**, 87–90.
16. Hafiz, M. and Abd-Shukor, R. (2015) Effect of nanosized NiF₂ addition on the transport critical current density of Ag-sheathed (Bi_{1.6}Pb_{0.4})Sr₂Ca₂Cu₃O₁₀ superconductor tapes. *Advances in Materials Science and Engineering*, 2015, **146476**.
17. Hagenmuller, P. (1985) Inorganic solid fluorides: Chemistry and Physics. *Academic Press, London*.

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- Impact of SnF₂ Addition on AC Susceptibility and Electrical Properties of Bi_{1.6}Pb_{0.4}Sr₂CaCu₂O₈ Superconductor
18. Portier, J., Reau, J. M., Matar, S., Soubeyroux, J. L. and Hagenmuller, P. (1983) Advances on fluorine ion conductors, basic and applied research. *Solid State Ionics*, **11(1)**, 83–90.
19. Sorokin, N. I. (2004) SnF₂-based solid electrolytes. *Inorganic Materials*, **40(9)**, 989–997.
20. Dénès, G. (1981) About SnF₂ stannous fluoride. IV. Kinetics of the $\alpha \rightarrow \gamma$ and $\beta, \gamma \rightarrow \alpha$ transitions. *Journal of Solid State Chemistry*, **37(1)**, 16–23.
21. Dénès, G. (1980) About SnF₂ stannous fluoride. VI. Phase transitions. *Materials Research Bulletin*, **15(6)**, 807–819.
22. Patro, L. N. and Hariharan, K. (2009) AC conductivity and scaling studies of polycrystalline SnF₂. *Materials Chemistry and Physics*, **116(1)**, 81–87.
23. Oboudi, S. F. & AL-Habeeb, M. Q. (2016) Gold Nanoparticles Effect on (Bi, Pb)-2223 Superconducting Thin Films. *Applied Physics Research*, **8(5)**, 64–74.
24. El Ghouch, N., Al-Oweini, R. & Awad, R. (2019) Synthesis, characterization and electrical properties of hybrid mono-iron-substituted undecatungstosilicate/(Bi, Pb)-2223 phase superconductors. *Materials Research Express*, **6(11)**, 116001.
25. Gopalakrishnan, I. K., Yakhmi, J. V. and Iyer, R. M. (1991) Stabilization of superconductivity in TlBa₂CuO_{5- δ} at 9.5 K and its enhancement to 43 K in TlBaSrCuO_{5- δ} . *Physica C: Superconductivity*, **175(1)**, 183–186.