J. Mountain Res. P-ISSN: 0974-3030, E-ISSN: 2582-5011 DOI: https://doi.org/10.51220/jmr.v21-S2.16
Vol. 21(S2), (2026) 132-139

Enhanced Structural, Microscopic, and Superconducting Properties of Ag-Doped (Tl,Bi)SrCaCuO High-Temperature Superconducting Films

A K Sharma*• Rupali Mishra • Surendra Singh

Deptt of Sciences, Quantum University, Roorkee-247167, Uttarakhand, India

*Corresponding Author's Email Id: ajay.asc@quantumeducation.in

Received: 21.02.2025; Revised: 19.10.2025; Accepted: 19.11.2025

Abstract: In this study, un-doped and Ag-incorporated (Tl,Bi)SrCaCuO high-temperature superconducting (HTSC) monolayer films were successfully deposited using the economically viable spray pyrolysis technique (SPT) on MgO(100) single-crystal substrates. The deposited films exhibited superconducting transition temperatures (Tc) ranging from 88.3 to 86.2 K, with a fine transition width of approximately 12 K. Structural characterization using X-ray diffraction (XRD) revealed the lattice parameters for un-doped (Tl,Bi)SrCaCuO as a = 3.8520 Å and c = 13.8630Å, while Ag-doped films exhibited slight variations, with a = 3.8120 Å and c = 13.8520 Å. The incorporation of Ag was found to enhance the critical current density (Jc) while slightly reducing the parameter of c-lattice. These results highlight the potential of doped Ag film in improving the superconducting properties, making them promising candidates for high-temperature superconducting applications.

Keywords: Ag-doped (Tl,Bi)-1223 film • Spray Pyrolysis Technique (SPT) • sharp transition width • lattice parameters • (Tl,Bi)SrCaCuO HTSC film.

Introduction

Tl-based superconducting films have unique and important feature compared to other HTSC's e.g. Y,(Cu,C)and Bi based cuprate superconductors in regard to occurrence of Tc from 80 K to 125 K and Jc values from ~ 10^4 to 10^6 A cm^{-2} (Kováč J et al (2022), Li Yugang et al (2024), Hellstrom E E et al (1992), Sundaresan A et al (2003) and Bhattacharya R N et al (2002)).

In recent years, superconducting Tl monolayer cuprates have garnered significant interest due to their higher irreversibility field as compared to double-layer Tl and Bi superconductors (Nabatame T et al (1993)). Since their discovery, superconducting wires and tapes based on this material family have been developed in high Tc. The $Tl_1Ba_2Ca_2Cu_3O_9$ (Tl-1223) phase is derived from Tl-1212 by the addition of a Ca layer and an extra CuO_2 plane. In both Tl-1212 and Tl-1223, the Tl-O chain plays a crucial role in transferring holes into the CuO_2 planes, regulating charge density by modulating the oxygen content (Li S et al (1991)).

Numerous research studies have been published on Bi-doped monolayer cuprates (Hopfinger T et al (2001), Goodman P et al (1993), Ren Z F and Wang J H et al (1993) and Torii Y et al (1990)). It has been reported that Bi can substitute Tl up to a maximum of 25%, beyond which additional Bi leads to the formation of impurities, primarily Bi-2201. While many researchers have considered the (Tl,Bi)SrCaCuO system to exhibit a similar structure to mono Tl-O layer in the 1212/1223 type, later investigations suggest it may shows an entirely new crystal structure. Therefore, determining the precise structure of (Tl,M)-O (where M = Bi, Pb, etc.) is crucial for gaining a deeper understanding of the material's physical properties (Torii Y, Kotani T et al (1989), Torii Y, Takei H et al (1989) and Dong C et al (1989)). .

The TlSrCaCuO (TSCCO) system forms new superconducting phases, including the TSCCO-1212 phase showing Tc of approximately 75 K and the TSCCO-1223 phase having Tc around 100 K (Matsuda S P et al (1988)). Unlike the TlBaCaCuO

(TBCCO) system, which contains a double Tl-O plane, the TSCCO system features a single Tl-O plane (Soeta A et al (1989)). Generally, the TSCCO system is metastable due to overdoping but can be stabilized through partial substitution of Bi at the Tl site. Researchers have reported that Bi substitution helps maintain superconducting phases with a single Tl-O layer structure. However, studies on the preparation of (Tl,Bi)SrCaCuO and Ag-incorporated (Tl,Bi)SrCaCuO remain limited (Przybylski K et al (2005) and Koo H S et al (2007)).

It is easy to fabricate the doped Tl-based film on different substrates like MgO, LAO, STO, YSZ, and ZrO_2 etc. and the quality of the films can be improved by optimizing the preparation techniques and post deposition annealing. The deposition of HTSC's film via sophisticated techniques like sputtering, e-beam evaporation and laser ablation etc. serves a smooth and high quality which are useful for microwave application. The conventional technique also used for the deposition of HTSC's films for the purpose of specific applications like SQUID, Light Detectors etc. Thus conventional film deposition technique like CVD, electrodeposition and spray pyrolysis etc. have an inherent potential for specific purposes.

In this study, (Tl,Bi)SrCaCuO and Ag-incorporated (Tl,Bi)SrCaCuO high-temperature superconducting (HTSC) films were fabricated using economically viable the spray pyrolysis technique on MgO (100) single-crystal substrates. The spray pyrolysis technique has been discussed in detail in previous chapters; here, we provide a brief overview of the specific approach used in this work.

Methodology :

(Tl,Bi)SrCaCuO and (Tl,Bi)SrCaCuO; Ag HTSC films were prepared in three step process, in order to take care of toxicity of thallium.

Precursor films of BiSrCaCuO and Ag-incorporated BiSrCaCuO were deposited on MgO (100) single-crystal substrates using the spray pyrolysis technique. In this process, an aqueous methanolic solution with a 0.3 M concentration was prepared using nitrates of bismuth, calcium, and copper in a stoichiometric ratio of 0.2:2:2.2:3 for BiSrCaCuO and 0.2:2:2.2:3:0.2 for BiSrCaCuAg. Triple-distilled water was used as the solvent, with methanol added at a ratio of 1 ml per 5 ml of nitrate solution to enhance the rapid separation of metal nitrates into oxides and facilitate solvent evaporation at the deposition temperature.

During the deposition substrate temperature was maintained at 500 ± 10°C. Initially, the temperature dropped by approximately 50°C at the onset of deposition but stabilized within a few minutes. Oxygen gas was used as the carrier, and the spray rate was maintained at approximately 1.6 ml/min. After deposition, the precursor film was gradually cooled to ambient temperature before being removed from the heater surface.

Annealing and Thallination :

In the second step, a systematic precursor annealing (prethallination) was carried out at 600 ±5 ^{0}C for 10 minutes in a PID controlled furnace. Precursor annealing was carried out in ambient condition. The temperatures of the furnace were programmed to increase till the required temperature of 600 ^{0}C by maintaining the rate of 6 ^{0}C /min. and remain stable for 10 minutes at the same temperature. After that furnace was cooled down at the rate of 2 ^{0}C per min. to 100 ^{0}C. After these films was taken out of the furnace in the ambient.

Precursor film annealing was carried out for complete dissociation of nitrates and to increase the crystallinity of the film and also texturing of the film. This step was done keeping in view of the coalescence of grains which has been reported to be beneficial in regard to Tc & Jc (Monot I et al (1992)).

The third and final step involves thallination of precursor films to get the superconducting phase by reaction of thallium vapour into the precursor film. In order to achieve this reaction, precursor film and thallium powder (Tl_2O_3) were put together in a tightly capped platinum box. The platinum box was enclosed within a silica tube, which was maintained under an oxygen atmosphere. The specially designed silica tube featured inlet and outlet ports for gas flow, along with a provision for a thermocouple to monitor the real-time temperature inside the tube. The thermocouple's tip was positioned near the platinum box to ensure precise temperature measurement at the site where thallium diffusion into the precursor film occurred in an oxygen-rich environment. The diffusion of thallium vapour into the precursor is highly dependent on the oxygen partial pressure and pressure of Tl_2O_3 vapour. For thallination process, the furnace temperature was set at 945^0C. The silica tube with all above arrangements was inserted into the furnace. The temperature of the silica tube quickly rises to the temperature of 905 ^{0}C within five minutes. At this temperature thallination process was performed for 2 minutes and then silica tube was pulled out of the furnace to room temperature and was allowed to cool down naturally.

Considering that the optimal temperature range for thallium diffusion into precursor films lies between 860°C and 910°C, an optimized temperature of 905°C was found to yield favorable superconducting properties in HTSC films using this process.

In this study, efforts were directed toward the preparation and characterization of (Tl,Bi)SrCaCuO and Ag-incorporated(Tl,Bi)SrCaCuO HTSC films. (Tl,Bi)SrCaCuO films from precursor BiSrCaCuO and Ag-incorporated BiSrCaCuO films through a two-step annealing process. To ensure precise thallination, the temperature near the platinum box was carefully regulated using a PID controller with an accuracy of ±2°C. Throughout the thallination process, an oxygen-rich atmosphere was maintained. Following the reaction, the films were rapidly quenched to ambient temperature. The Tl:HTSC films were then extracted from the silica tube and subjected to various characterization techniques.

Characterization of (Tl,Bi)SrCaCuO and Ag Incorporated (Tl,Bi)SrCaCuO HTSC films:

The as-deposited films underwent a series of investigations to determine their structural and microstructural characteristics. The crystal parameters were analyzed using X-ray diffraction (XRD) with a Rigaku instrument employing Cu Kα radiation. The film morphology and composition were examined using a Scanning Electron Microscope (SEM) coupled with an Energy-Dispersive X-ray spectrometer (EDAX), specifically the JEOL-JSM 5600 model.

Electrical resistivity was measured using the standard four-probe method following the Van der Pauw technique, with a Keithley instrument providing a precise constant current source and voltmeter. The zero-field DC transport critical current density (Jc) was determined using a 1 μV/cm criterion, where a bridge pattern (1 mm length, 0.5 mm width) was manually created by removing the undesired film area from the substrate with a sharp-edged blade.

RESULT AND DISCUSSION :

The present work have been carried out to outline the following results –

(i) To prepare the (Tl,Bi)SrCaCuO HTSC film by spray pyrolysis technique on MgO (100) single crystal substrate.

(ii) To study the effect of Ag incorporation on

Structural and microstructural characterization of (Tl,Bi)SrCaCuO and Ag incorporated (Tl,Bi)SrCaCuO films :

Structural and microstructural characterization of the as deposited films of (Tl,Bi)SrCaCuO and Ag incorporated (Tl,Bi)SrCaCuO were carried out by a number of investigations. The

XRD pattern for (Tl,Bi)SrCaCuO film shown in Figure-1.1 (a). The presence of peaks (102), (004) (103), (110), (107), (201), (115), (106), (203), (204) and (214) of the dominant 1223 phase together with reflections like (003) and, (112) for 1212 minority phase are indicative of the multiphasic nature of the film. The presence of a few (00*l*) peaks is indicative of partially oriented nature of the film. Similarly XRD patterns for (Tl,Bi)SrCaCuO; Ag film shown in Figure-1.1 (b) indicates an Ag peak at $2\theta = 38.7^0$ of (111) phase.

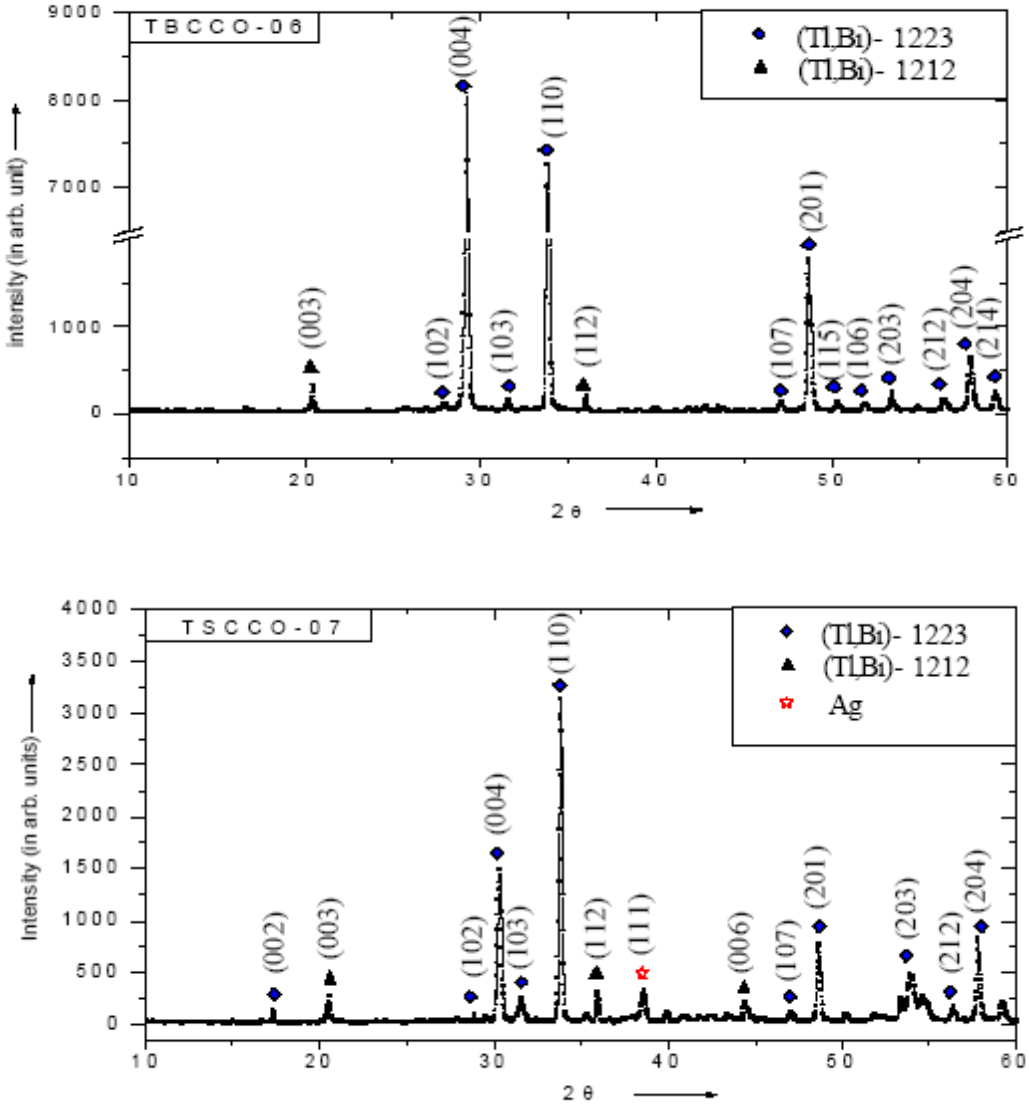

Figure 1.1 (a), (b) XRD pattern of (Tl,Bi)SrCaCuO and silver incorporated (Tl,Bi)SrCaCuO HTSC films shows the (Tl,Bi)-1223 majority phase and (Tl,Bi)-1212 minority phase for both the films. The lattice parameters have been calculated by POWD programme resulting the value 'a' and 'c' are 3.8520 Å and 13.8630Å respectively for (Tl,Bi)SrCaCuO and 'a' and 'c' are 3.8120 Å and 13.8520 Å respectively for Ag assimilated (Tl,Bi)SrCaCuO film.

Measurement of Transition Temperature (Tc) and Critical Current Density (Jc) of As-Deposited HTSC Films:

The superconducting transition temperature of the both films were determined by using Four Probe method of Vander Pauw technique using sensitive constant current source and

voltmeter of Kiethely instrument. The Tc (R=0) of the Ag free and Ag-incorporated (Tl,Bi)SrCaCuO HTSC films are 88.3 K and 86.2 K respectively and transition width ~ 11 K and ~9 K respectively as shown in Figure-1.2 (a), (b). This result shows that the sharp transition occur in (Tl,Bi)SrCaCuO HTSC films. The criticalcurrentdensity ~ 2.34 × 10^4 A cm^{-2} for (Tl,Bi)SrCaCuO and ~ 2.34 × 10^4 A cm^{-2} for Ag-incorporated (Tl,Bi)SrCaCuO film has been calculated by making a pattern of 1.0 mm in length and 0.5 mm in width with criterion of 1.0 μV/cm.

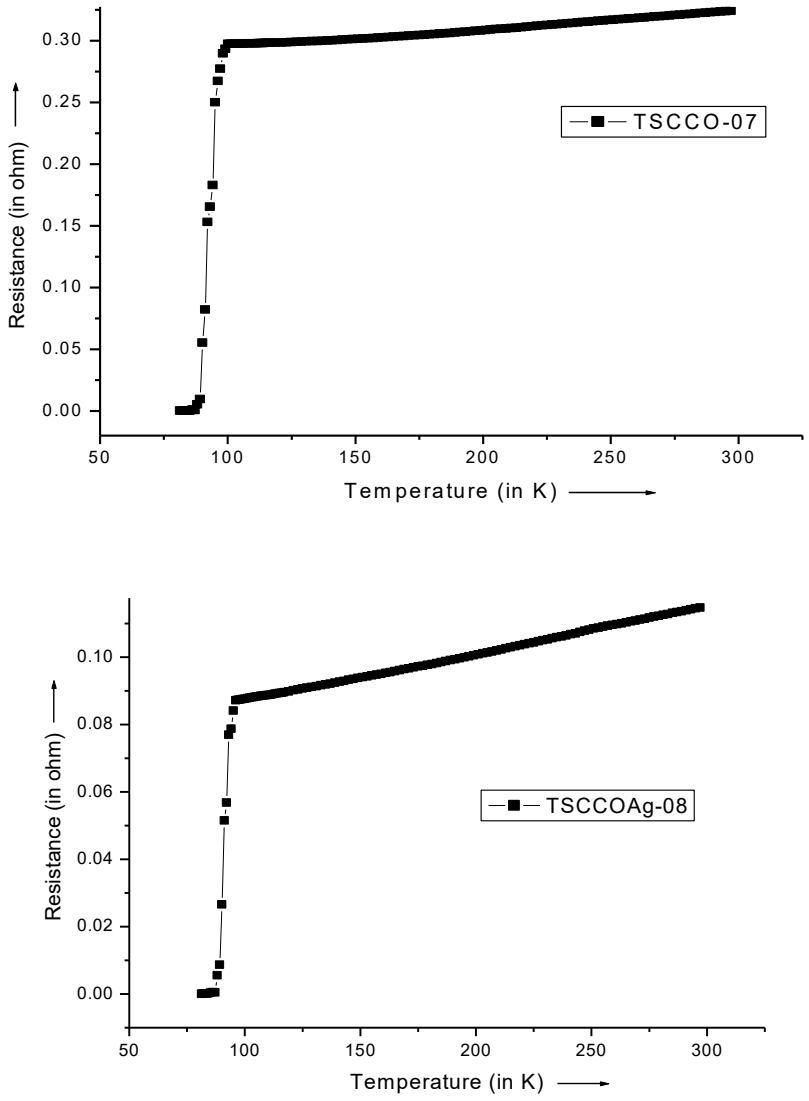

Figure- 1.2 (a), (b) Resistance versus temperature curve for (Tl,Bi)SrCaCuO and silver incorporated (Tl,Bi)SrCaCuO HTSC films on MgO (100) substrate exhibiting Tc (R=0) ~ 88.3 K and Tc (R=0) ~ 86.2 K for Ag free and Ag incorporated films respectively.

Composition and Scanning Electron Microscopic (SEM) Analysis :

It has been observed that the overall intensity of the XRD pattern decreases by Ag incorporated (Tl,Bi)SrCaCuO films. The composition ratio of Tl:Bi:Sr:Ca:Cu and Tl:Bi:Sr: Ca:Cu:Ag to 0.9 : 0.3 : 1.8 : 1.6 : 3.0 and 0.9 : 0.2 : 1.8 : 1.6 : 3.0 : 0.18 respectively that exhibit stoichiometric nature of the film which is in conformity with XRD result, which shows a mixture of superconducting and non superconducting phases.

Figure-1.3 (a), (b) shows the SEM analysis of the (Tl,Bi)SrCaCuO and Ag incorporated (Tl,Bi)SrCaCuO HTSC films prepared on MgO (100) single crystal substrate and processed at thallination temperature of 905^0 C for 2 minutes. This shows the presence of small unoriented platy crystallines ~ 5 μm in size whereas in case of Ag incorporated (Tl,Bi)SrCaCuO HTSC film along oriented platy crystallites are appreciably noticeable. It may be stipulated that Ag helps to get a strong attraction between the molecules within the films causes an oriented growth in crystallites as is observed in Ag incorporated sample. Both films exhibit a well connected, smooth morphology and dense nature of the films.

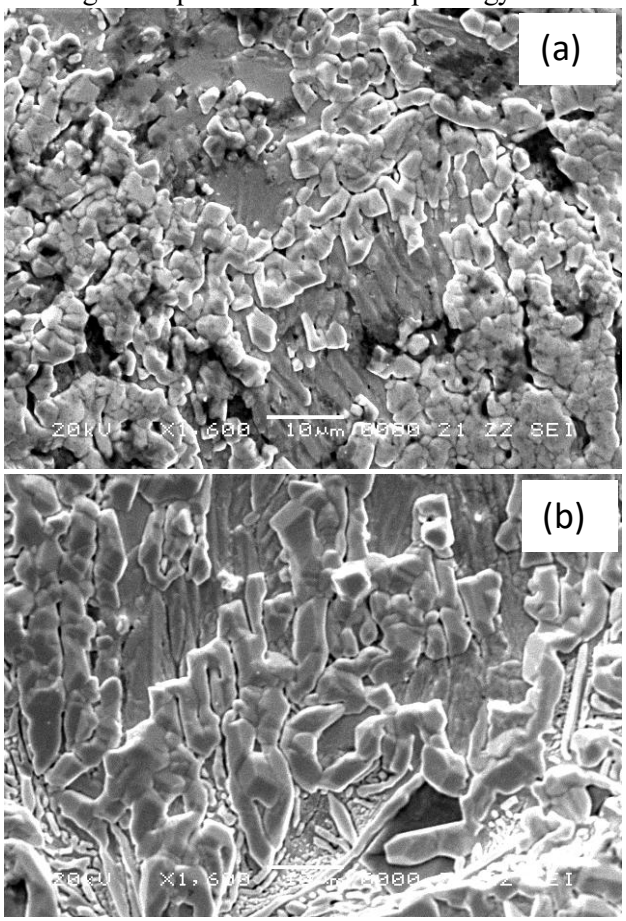

Figure-1.3 (a), (b)Scanning Electron Micrographs of (Tl,Bi)SrCaCuO and silver incorporated (Tl,Bi)SrCaCuO HTSC films exhibits the small unoriented platy crystallines for Ag free and large, oriented platelet shaped crystallites for Ag incorporated films respectively.

Effect of silver (Ag) incorporation on film characterization :

Keeping in view the fact that silver addition in the film may enhance critical current density (Jc). We studied the effect of silver addition in (Tl,Bi)SrCaCuO film on transition temperature (Tc), critical current density (Jc) and micrographical features.

Silver addition in TlBaCaCuO HTSC film enhances the critical current density (Jc). Therefore we have also studied the effect of silver addition in (Tl,Bi)SrCaCuO HTSC films, we added silver in 0.2 molar ratio.

Critical Transition Temperature (Tc)-

It has been found that 0.2 molar ratio addition of silver in the (Tl,Bi)SrCaCuO film did not affect the Tc values as it remain approx. same Tc (R=0) ~ 86.2 K. Figure –1.2 (b) shows the resistance versus temperature profile of the silver (0.2 molar ratio) containing (Tl,Bi)SrCaCuO HTSC film on MgO (100) substrate. The curve shows the good metallic behaviour of the film before Tc (onset). It has

been also observed that the surface resistance of the film also decreases due to incorporation of silver (Ag).

Critical Current Density (Jc)-

It has been found that these in a fractional increase in the critical density (Jc) compared to the silver free (Tl,Bi)SrCaCuO HTSC films. The Jc value increased from ~ 2.34 × 10^4 A cm^{-2} for (Tl,Bi)SrCaCuO film to ~ 2.81 × 10^4 A cm^{-2} for silver containing (Tl,Bi)SrCaCuO film by addition of 0.2 molar ratio.

Xray diffraction investigation –

Figure – 1.1 (b) shows the XRD pattern of the 0.2 molar ratio silver added (Tl,Bi)SrCaCuO HTSC film on MgO (100) substrate. This pattern shows the formation of 1223 phase with c = 13.8520 Å. The occurrence of silver peak in XRD pattern near 2θ = 38.7 ^{0} is indicative of the presence of Ag in the film.

Scanning Electron Microscopy investigation –

Figure – 1.3 (b) represent the scanning electron micrograph of the 0.2 molar ratio Ag added (Tl,Bi)SrCaCuO HTSC film. This photograph clearly exhibits the large and oriented platelet shaped crystallites.

Conclusion

In the present report (Tl,Bi)SrCaCuO and Ag assimilated (Tl,Bi)SrCaCuO HTSC films with nominal composition (Tl,Bi)SrCaCuO and (Tl,Bi)SrCaCuO Ag have been synthesized successfully by using a rather economically viable spray pyrolysis technique on MgO (100) single crystal substrate. The deposited films shows Tc (R=0) ~ 88.3 K and ~ 86.2 K for (Tl,Bi)SrCaCuO and Ag incorporated (Tl,Bi)SrCaCuO HTSC films respectively. The R-T measurement shows a sharp transition for Ag incorporated sample compared to Ag free sample having value ~9 K and ~12 K respectively.

The results indicate that the films exhibit good metallic behavior. X-ray diffraction (XRD) analysis confirms the presence of a dominant (Tl,Bi)SrCaCuO-1223 phase, along with a minor fraction of the (Tl,Bi)SrCaCuO-1212 phase. The lattice constants, determined using the POWD program based on experimental d-values, were found to be a = 3.8520 Å, c = 13.8630Å for (Tl,Bi)SrCaCuO and a = 3.8120 Å, c = 13.8520 Å for Ag-incorporated (Tl,Bi)SrCaCuO HTSC films.

A noticeable decrease in the c-lattice parameter was observed in the Ag-incorporated films compared to the Ag-free (Tl,Bi)SrCaCuO films, suggesting that Ag incorporation contracts the c-unit parameter. This structural modification correlates with an increase in the critical current density (Jc) of the Ag-incorporated films, demonstrating an enhancement in their superconducting properties compared to Ag-free samples.

References :

Bhattacharya R N, Xing Z, Wu J Z, Chen J, Yang S X, Ren Z F, and Blaugher R D (2002) Superconducting thallium oxide and mercury oxide films. Physica C: Superconductivity, 377, 327-332.

Dong C, Sheng Z Z, Fei X, Sheng L, Wang J H, and Hermann A M (1989) SUPERCONDUCTIVITY ABOUT 120 K IN THE TI-Bi-Sr-Ca-Cu-O SYSTEM. Physica C: Superconductivity, 161, 257-261.

Goodman P, Marks R, Nexhip C, O'Donnell T A, and Miller P (1993) Investigation of 1223 and 1122 (Tl, Bi)CaSrCuO compounds using neutron powder diffraction. Physica C: Superconductivity, 217, 325-334.

Hellstrom E E (1992) Important Considerations for Processing Bi-Based High-Temperature Superconducting Tapes and Films for Bulk Applications. MRS Bulletin, 17, 45-51.

Hopfinger T, Lomello-Tafin M, Jorda J L, Galez P, Couach M, Gladyshevskii R E, and Soubeyroux J L (2001) Unsubstituted Tl-1223: a possible candidate for high current

applications. Physica C: Superconductivity, 351, 53.

Koo H S, Ku H K, Chen M, and Kawai T (2007) Tl-Ba-Ca-Cu-O system prepared by spray pyrolysis and Tl-diffusion. Physica C: Superconductivity, 455, 71-75.

Kováč J, Chromik Š, Hušek I, and Šefčík D (2022) Effect of Silver Doping on the Superconducting and Structural Properties of YBCO Thin Films on Buffered Ni-W Tapes. Materials, 15, 5354.

Li S, Greenblatt M, Jeon Y, Chen J, Liang G, and Croft M (1991) X-ray absorption near-edge structure study of copper valency in the superconducting Tl-Ca-Ba-Cu-O and Bi-Ca-Sr-Cu-O phases. Physica C: Superconductivity, 173, 239.

Li Yugang, Liu Zhiyong, Zhu Ping, He Jinyu, and Cai Chuanbing (2024) High-Temperature (Cu,C)$Ba_2Ca_3Cu_4O_y$ Superconducting Films with Large Irreversible Fields Grown on $SrLaAlO_4$ Substrates by Pulsed Laser Deposition. Crystals, 14, 514.

Matsuda S P, Takeuchi S, Soeta A, Suzuki T, Aihara K, and Kamo T (1988) Superconductivity of Tl-Sr-Ca-Cu-O System in Relation to Tl-Ba-Ca-Cu-O System. Japanese Journal of Applied Physics, 27, 2062.

Monot I, Lepropre M, Provost J, Desgardin G, and Raveau B (1992) High performance in a bulk melt-textured $YBa_2Cu_3O_{7-\delta}$ ceramic. Superconductor Science & Technology, 5, 712-718.

Nabatame T, Saito Y, Aihara K, Kamo T, and Matsuda S P (1993) Comparison of Transport Properties between Tl-(1223) and Tl-(2223) Phases of Tl-Ba-Ca-Cu-O Systems. Japanese Journal of Applied Physics, 32, L484.

Przybylski K, Heims O, and Gritzner G (2005) Synthesis of $TlBa_2Ca_2Cu_3O_9$ superconducting ceramics by solid state reaction in Tl2O atmosphere. Physica C: Superconductivity, 423, 63.

Ren Z F and Wang J H (1993) Enhanced formation of 1223 phase by partial replacement of Bi for Tl in in-situ synthesized silver-sheathed superconducting tape of $Tl_{1-x}Bi_xSr_{2-y}Ca_2Cu_3O_{9-\delta}$. Physica C: Superconductivity, 216, 199-204.

Soeta A, Suzuki T, Takeuchi S, Kamo T, Usami K, and Matsuda S P (1989) Relationship between Crystal Structures and Solid Solution of Tl-Sr-Ca-Cu-O System. Japanese Journal of Applied Physics, 28, L1186.

Sundaresan A, Asada H, Crisan A, Nie J C, Kito H, Iyo A, Tanaka Y, Kusunoki M, and Ohshima S (2003) Preparation of Tl-2212 and -1223 superconductor thin films and their microwave properties. Physica C: Superconductivity, 388, 473-474.

Torii Y, Kugai H, Takei H, and Tada K (1990) Preparation of Ag-Sheathed (Tl, Bi)-Ca-Sr-Cu-O Superconducting Wire. Japanese Journal of Applied Physics, 29, L952.

Torii Y, Kotani T, Takei H, and Tada K (1989) Superconductivity in the Tl-Bi-Ca-Ba-Cu-O and Tl-Bi-Ca-Sr-Cu-O Systems. Japanese Journal of Applied Physics, 28, L1190-L1192.

Torii Y, Takei H, and Tada K (1989) Superconductivity in Tl-Bi-Ca-Sr-Cu-O and Tl-Bi-Pb-Ca-Sr-Cu-O Systems. Japanese Journal of Applied Physics, 28, L2192.