dian J. Phys. 76A (1), 95-99 (2002)

IJP A
an international journal

Synthesis and microstructural characteristics of Tl-based high temperature superconducting tapes

B Das[1], G D Verma[2]** and O N Srivastava[3]*

[1] Department of Solid State Physics and Electronics, Dr R M L Avadh University, Faizabad-224 001, Uttar Pradesh, India
[2] School of Pure and Applied Physics, Guru Ghasidas University, Bilaspur-495 009, Madhya Pradesh, India
[3] Department of Physics, Banaras Hindu University, Varanasi-221 005, Uttar Pradesh, India

E-mail : ons@banaras.ernet.in

Abstract The superconducting tapes of Tl-Ba-Ca-Cu-O HTSC system were synthesised through doctor blade tape casting process. Their structural-microstructural characteristics were explored through X-ray diffraction (XRD) and transmission electron microscopic (TEM) techniques. A novel feature of the present synthesis route was that here in the same thallination process, tapes of two different HTSC phases possessing single and double Tl-O layers *i.e.* $TlBa_2CaCu_2O_7$ (1212) and $Tl_2Ba_2CaCu_2O_8$ (2212) or $TlBa_2Ca_2Cu_3O_9$ (1223) and $Tl_2Ba_2Ca_2Cu_3O_{10}$ (2223), could be synthesised. The transition temperatures (T_c's) of the as synthesised tapes were found in the range of ~ 80 – 115K.

Keywords Tl-based HTSC tapes, synthesis, micro-structural characteristics

PACS Nos. 74.72.Fq, 85.25.Kx

1. Introduction

Since the discovery of superconductivity at ~ 35K in the La-Ba-Cu-O system by Bednorz and Muller [1], many other cuprate superconductors such as Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O, Tl-Ba-Ca-Cu-O and Hg-Ba-Ca-Cu-O [2-5] with superconducting transition temperatures (T_c's) above liquid nitrogen temperature, have been discovered. However, practical applications of these materials have been hampered by two major difficulties : the low critical current density (J_c) and the poor mechanical properties. These two problems are indirectly associated with the granular nature of these materials. The first requirement for large scale applications of these HTSC materials is that the materials be available in polycrystalline form which is not electromagnetically granular. Unfortunately, all the high T_c cuprate superconductors, except Bi-based, are electromagnetically granular in all fields. However, Tl-based superconductors with monolayer of Tl-O appear to have high current carrying capacity in high magnetic fields due to comparatively closely spaced CuO_2 layers in these materials [6,7]. Thallium is also known to passivate the grain boundary and hence increases the intergrain critical current density (J_c).

Corresponding Author
* Present address : Department of Physics, IIT Roorkee, Roorkee-247 667 (U. A.), India.

Another problem concerning with the brittleness of HTSC materials, can be overcome by fabricating metal/superconductor composites, such as metal-clad wires, tapes and multifilaments [8, 9]. Furthermore, the metal (*e.g.* silver) provides a means of thermal dissipation, thus stabilising the superconductor's environment.

The doctor blade process (DBP) [10], among the various methods to produce metal/superconductor composites, has proved to be an attractive route for producing very long homogeneous superconducting tapes/wires. However, despite the known facts regarding the superiorities of thallium based cuprate superconductors *e.g.* the occurrence of higher T_c's in this system (T_c ~ 127K for Tl : 2223 phase [11]) and the fact that excess Tl can passivate the grain boundaries and thus minimise weak link effects, rather sparse studies have been made in the case of Tl-Ba-Ca-Cu-O tapes/wires. Only some studies on Tl bearing cuprate HTSC tapes, employing the powder in tube (PIT) method, have been done so far [12-14]. However, synthesis and formation of Tl : HTSC tapes through the other well known technique – the doctor blade process does not seem to have been carried out so far.

Keeping these facts in view, we have employed the doctor blade process for synthesis of Tl-bearing HTSC tapes in the

present investigations. We have also explored their superconducting and structural/ microstructural characteristics. A novel feature of the present synthesis method relates to the fact that here in the same thalliation process, tapes of two different HTSC phases possessing single and double Tl-O layers *i.e.* $TlBa_2CaCu_2O_7$ and $Tl_2Ba_2CaCu_2O_8$ or $TlBa_2Ca_2Cu_3O_9$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$, could be synthesised

2. Experimental methods

In the present investigation, the Tl-based cuprate tapes have been prepared by following a three-steps process. The salient features of this are described below.

First of all, precursor oxide powder of nominal compositions $Ba_2CaCu_2O_x$ and $Ba_2Ca_2Cu_3O_z$ have been prepared by standard ceramic method [15, 16]. In the second step, the slip was prepared by mixing thoroughly the precursor powder with fish oil and then stirring with an organic formulation consisting of a solvent (ethyl alcohol and trichloroethylene), binder (polyvinyl butyral) and plasticizer (polyethylene glycol + octylthalate). The resulting viscous fluid was finally cast under a doctor blade onto the carrier sheet (cellulose film), producing a green tape of 1.00 cm wide.

The typical thickness of the as cast tape was about 200 μm. Small precursor tape (Ba-Ca-Cu-O) of 10 mm long and 5 mm wide cut from the green tape was slowly heated (2°C/min.) to 500°C for 3h. and then cooled slowly (2°C/min.) to remove the organic compounds from the precursor tape and to avoid the crack formation inside the tapes. Finally in the 3rd step, the dried precursor (Ba-Ca-Cu-O) tapes were thalliated under Tl_2O_3 vapour in the two different configurations which are described below.

2.1 Configuration-1 :

In this configuration, appropriate amount of Tl_2O_3 powder was taken in a platinum box and a precursor tape labeled as *A* or *A′* (*A*/*A′*) was kept above (~ 2 mm) the Tl_2O_3 powder as shown in Figure 1(a). Here the precursor tape labeled as *A* corresponded to composition $Ba_2CaCu_2O_x$ and *A′* to $Ba_2Ca_2Cu_3O_z$. The closed platinum box containing Tl_2O_3 and precursor tape was transferred into a silica tube attached with an oxygen flowing system. Finally, it was kept in a preheated programmable Heraeus furnace at 900 ± 1°C for about 12-15 min in the flowing oxygen and allowed to cool at the rate of 2°C min upto room temperature.

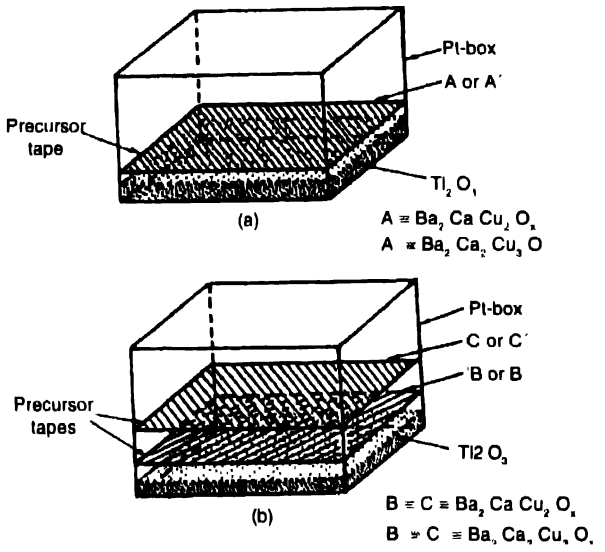

Figure 1. Configurations of thalliation of precursor tapes.

2.2 Configuration–2 :

In this configuration, two precursor tapes either *B* and *C* or *B′* and *C′* were kept above the Tl_2O_3 powder as shown in Figure 1(b). Here, the precursor tapes *B* and *C* correspond to composition $Ba_2CaCu_2O_x$; on the other hand *B′* and *C′* $Ba_2Ca_2Cu_3O_z$. The tapes *B* or *B′* *i.e.* (*B*/*B′*) were just above the Tl_2O_3 (~ 2 mm) and *C* or *C′* (*C*/*C′*) above the tape *B*/*B′* as shown in Figure 1(b). The closed platinum box containing Tl_2O_3 and precursor tapes with above mentioned configuration was kept inside the silica tube for thermal treatment. The thermal treatment was similar to configuration-1.

The gross phase identification of the as synthesised HTSC tapes was carried out with a Philips PW-1710 diffractometer having a wide angle goniometer fitted with a graphite monochromator employing Cu-Kα radiation. The variation of resistance with temperature of the tapes was measured by standard four probe method employing the van der Pauw technique. The current was supplied from a computer controlled Keitheley programmable constant current source (Model-220) and the voltage was measured by a Keitheley nanovoltmeter (Model–181). The sample was cooled by using a APD closed cycle chiller.

Since X-ray diffraction (XRD) reveals only the gross structures of the materials, the necessity of carrying out electron microscopic investigation for uncovering the structural microstructural characteristics at the microlevel (nanometer dimensions) is evident. In order to achieve this goal, computerised Philips electron microscope (EM CM-12) was used in imaging and diffraction modes.

3. Results and discussion

After the thalliation of the precursor tapes under the configurations mentioned earlier, the thalliated tapes were subjected to X-ray diffraction study for gross structural characterisation and identification of HTSC phases present in the as thalliated tapes. The X-ray diffraction patterns of the thalliated tapes *A* and *A′* are shown in Figure 2(a) and (b) respectively. The analysis of the XRD peaks corresponding to tape *A* [Figure 2(a)] revealed the presence of phase having bodycentred tetragonal lattice structure with $a = b = 3.86$ Å and $c = 29.31$ Å. On the other hand analysis of XRD peaks corresponding to tapes *A′* [Figure 2(b)] revealed the presence of phase having body-centred tetragonal lattice structure with $a = b = 3.86$ Å and $c = 35.95$ Å.

These results suggest that the thalliation of the tape A / A' d to the formation of double Tl-O layers compound

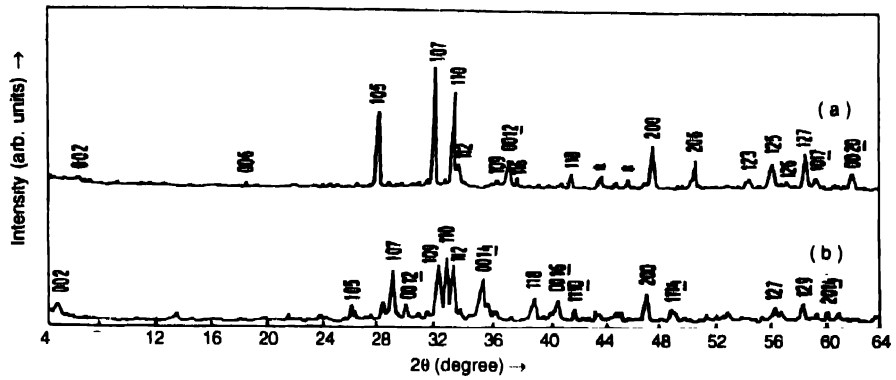

Figure 2. X-ray diffraction patterns of (a) the thalliated tape A showing the presence of dominantly $Tl_2Ba_2CaCu_2O_8$ HTSC phase and (b) the thalliated tape A revealing the presence of dominantly $Tl_2Ba_2Ca_2Cu_3O_{10}$ HTSC phase (* represents impurity phases.)

$_2Ba_2CaCu_2O_8$ /$Tl_2Ba_2Ca_2Cu_3O_{10}$. Similarly based on the XRD sults, it was found that thalliation of the tape B / B' which ere just above (~ 2mm) that Tl_2O_3 powder [Figure 1(b)], led to

for double Tl-O layers (2212, 2223) HTSC tapes at 77 K and zero field. It was noticed that T_c of the tapes B/B' (which were close to the Tl_2O_3 powder at a distance of ~ 2mm) was higher than the tapes C/C′ (which were some what away from Tl_2O_3 powder).

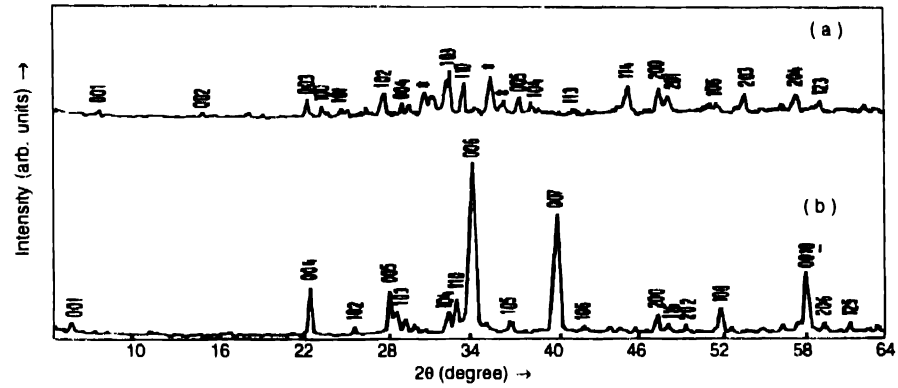

Figure 3. X-ray diffraction patterns of (a) the thalliated tape C revealing the presence of $TlBa_2CaCu_2O_7$ HTSC phase and (b) the thalliated tape C', showing the presence of dominantly $TlBa_2Ca_2Cu_3O_9$ HTSC phase. (* represents impurity phases)

ic formation of double Tl-O layers compounds (Tl : 2212/2223). he XRD patterns of the thalliated tapes C and C' have been own in Figure 3(a) and (b) respectively. The analysis of these atterns revealed that thalliation of the tape C led to the formation $TlBa_2CaCu_2O_7$ ($a = b = 3.85$ Å, $c = 12.75$ Å) HTSC phase and at of C' to $TlBa_2Ca_2Cu_3O_9$ ($a = b = 3.85$ Å and $c = 15.85$ Å).

From $R-T$ monitoring, the transition temperatures (T_c's) of e as synthesised tapes were found to be in the range of 80 – 15 K. The R–T curves corresponding to Tl- bearing HTSC tapes beled as A and A' have been shown in Figure 4. The T_c (R =) for tape A was ~ 102 K [Figure 4(a)] and for tape A' ~ 110 K igure 4(b)]. Similarly T_cs (R = 0) for thalliated tapes B and B' orresponded to ~ 99 K and 107 K respectively; and for thalliated pes C and C' ~ 87 K and 105 K respectively.

Transport critical current density (J_c) was also measured for e as synthesised tapes following the criterion of 1μV/cm. The ypical values of J_c's for the as synthesised tapes were ~ 7×10^4 /cm^2 for monoTl-O layer (1212, 1223) and ~ 4×10^4 A/cm^2

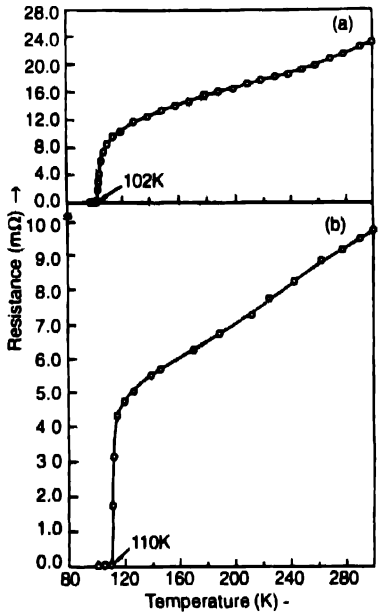

Figure 4. Resistance *vs* temperature curves of (a) the thalliated tape A and (b) the thalliated tape A'

The microstructural characteristics of the as thalliated tapes under configurations 1 and 2 as described in Sections 2.1 and 2.2 were studied by a transmission electron microscope using its various modes such as imaging, selected area diffraction (SAD) and convergent beam electron diffraction (CBED). Figure 5(a) shows a representative selected area electron diffraction pattern bringing out a^*–c^* reciprocal lattice net taken from the sample of the thalliated tape labeled as A. The analysis of the

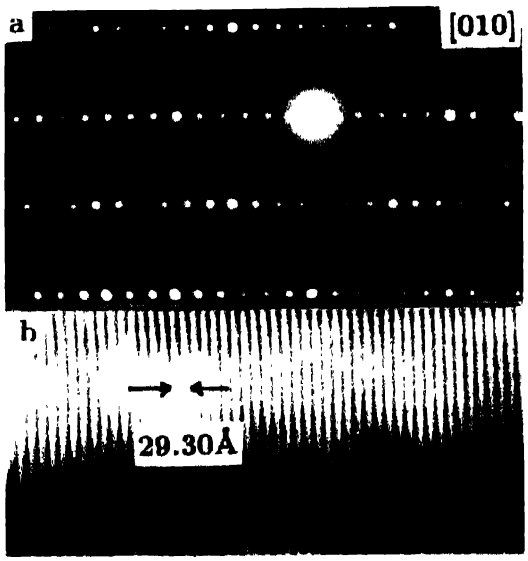

Figure 5. (a) [010] SAD pattern of the thalliated tape *A*, revealing the tetragonal phase with a = 3.86 Å and c = 29.30 Å corresponding to 2212 phase and (b) HREM of the thalliated tape *A* depicting *ool* planes. The fringe spacing of 29.30 Å corresponds to c periodicity of 2212 phase

pattern revealed the presence of tetragonal phase with a = 3.86Å and c = 29.30 Å. The c-periodicity of 29.30 Å was also substantiated by the presence of lattice fringes of spacing ~ 29.30 Å in the high resolution electron micrograph [Figure 5(b)] depicting *ool* planes taken from the specimen of the tape labeled as A. These lattice parameters correspond to Tl : 2212 phase

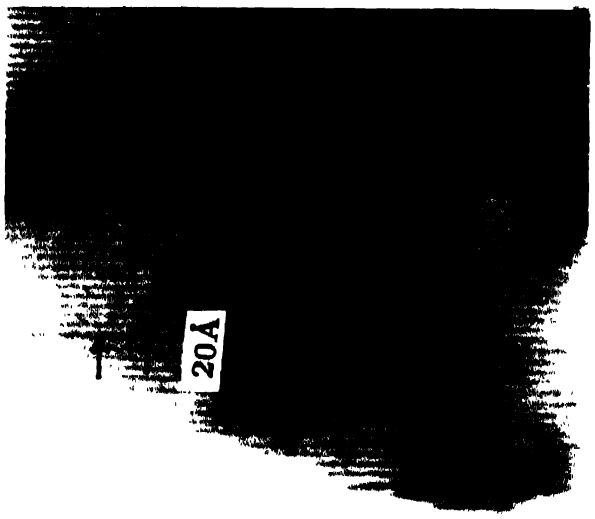

Figure 6. HREM of Tl bearing HTSC tape exhibiting the presence of stacking faults. The width of the fault is ~ 20 Å

These findings are in conformity with the X-ray diffraction results. Similarly, TEM explorations of the samples of thalliated tapes *A'*, *B/B'* and *C/C'* revealed the same structural features as obtained through XRD investigations. The TEM explorations also revealed the presence of stacking faults in the as synthesised tapes. Figure 6 represents the illustrative example of the observed stacking faults (marked by arrows). It may be noted that the typical width of stacking faults is around 20 Å. This is compatible with coherence length; therefore, these stacking faults may serve as flux- pinning centres.

The above studies revealed that tapes of both single Tl-O as well as double Tl-O layers compounds could be synthesised through the precursor tapes suitably exposed, in a single thalliation process. Both single Tl-O layer and double Tl-O layers compounds have their own merits in regard to their application potentiality. The double Tl-O layers compounds generally show higher T_c as compared to their corresponding (having same number of CuO_2 layers) single Tl-O layer compounds. One main advantage of the double layers HTSC system such as Bi : 2212 and 2223 is that the double layers of HTSC phases correspond to van der Wall platelet like solid, where we have aligned and electromagnetically connected grain morphology leading to high grain to grain J_c value. On the other hand, single Tl-O layer compounds appear to have higher current carrying capacity in high magnetic fields due to comparatively closely spaced CuO_2 layers in these materials.

4. Conclusions

In the present investigations we have successfully synthesised the tapes of HTSC phases of Tl-Ba-Ca-Cu-O system through doctor blade process and the synthesis was so tailored that based on the same thalliation process, both the double and single Tl-O bearing HTSC phases corresponding to either 2212 and 1212 or 2223 and 1223 could be synthesised. The R - T monitoring of the tapes thalliated under different configurations showed T_c's in the range of 80 –115K. The representative transport critical current density for the tapes synthesised in the present investigation was ~ 7×10^4 A/cm^2 for mono Tl-O layer (1212 and 1223) and ~ 4×10^4 A/cm^2 for double Tl-O layers (2212 and 2223) HTSC tapes. Based on both the XRD and TEM studies it has been found that the thalliation of the precursor tapes labeled as *A/A'* and *B/B'* which were in close proximity of the Tl_2O_3 powder (at a height of ~ 2 mm) lead to the formation of double Tl-O layer compound of Tl-Ba-Ca-Cu-O system, namely Tl:2212 and 2223. On the other hand, the thalliation of the tapes labeled as *C/C'* which were some what farther (at a height of ~ 4 mm) from Tl_2O_3 powder leads to the formation of single Tl-O layer compounds of Tl-Ba-Ca-Cu-O HTSC system, namely Tl : 1212 and 1223.

Acknowledgments

The authors are grateful to Prof. A. R. Verma, Prof. R. P. Rastogi and Prof. Yash Pal for encouragement. Extensive discussions with Prof. V. G. Bhide, Dr. A. V. Narlikar, Prof. T. V. Ramakrishnan,

Prof. R. K. Singh and Dr. B. A. Dasannacharya are gratefully acknowledged. The present work was financially supported by the University Grants Commission and N.S.T.B. (the Department of Science & Technology).

References

[1] J G Bednorz and K A Muller *Z Phys* **B64** 188 (1986)

[2] M K Wu, J R Ashuburn, C J Torng, P H Hor, R L Meng, L Gao, Z J Huang, Y Q Wang and C W Chu *Phys Rev. Lett.* **58** 908 (1987)

[3] H Maeda, Y Tanaka, M Kukutomi and A Asano *Jpn J Appl Phys* **27** 209 (1988)

[4] Z Z Sheng and A M Hermann *Nature* **332** 138 (1988)

[5] S N Putilin, E V Antipov, O Chmaissen and M Marezio *Nature* **362** 226 (1993)

[6] D H Kim, K E Gray, R T Kampwirth, J C Smith, D S Richeson, T J Mark, J H Kang, J Talvacchio and M Eddy *Physica* C **177** 431 (1991)

[7] R S Liu, D N Zheng, L W Loram, K A Mirza, A M Cambell and P P Edwards *Superconducting News* **6 Jan.** 1 (1992)

[8] T Hikata, T Nichikawa, H Mukai, K Sato and Hiotsuyanayi *J Appl. Phys* **28** 288 (1989)

[9] S X Dou, H K Liu, J Wang, M H Apperely, C C Sorrell, S J Guo, B Loberg and K E Easterling *Physica* C **172** 63 (1990)

[10] K Togano, H Kumakura, H Maeda, E Yanagisawa, N Irisawa, Shomoyawa and T Morimoto *Jpn J Appl. Phys.* **28** L95 (1990)

[11] T Kaneko, H Yamauchi and S Tanaka *Physica* C **178** 377 (1991)

[12] B A Glowacki and S P Ashworth *Physica* C **200** 140 (1992)

[13] J G Hu, D J Miller, K C Goretta and R B Poeppel *IEEE Transactions on Applied Superconductivity* **3** 1215 (1993)

[14] P J Kung, P G Wahlbeck, M E McHenry, M P Maley and D E Peterson *Physica* C **220** 310 (1994)

[15] I K Gopalakrishnan, PVPSS Sastry, K Gangadharan, G M Phatak, J V Yakhmi and R M Iyer *Appl Phys Lett* **53** 414 (1988)

[16] G D Verma, K Ramakrishna and O N Srivastava *Physica* C **202** 327 (1992)