Enhancement of T_c (~ 103 K) in calcium-free $\text{Tl}_2\text{Ba}_2\text{CuO}_x$ (2201) compound

K K SAINI, C P SHARMA, S N EKBOTE, PAVAS ASTHANA,
D K SURI, CHANDERKANT, S A AGNIHOTRY and
SUBHAS CHANDRA

National Physical Laboratory, Dr K S Krishnan Road, New Delhi 110012, India

Abstract. Enhanced T_c in calcium-free Tl compounds of the series $\text{Tl}_m\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$ (2201) has been reported. Three different starting compositions (2201, 1201 and 2202) were studied extensively with varying conditions of preparation. Under optimized conditions (sintering temperature 970°C and duration 3–10 min) the highest T_c (onset) ranges from 103 K to ~ 115 K and T_c (zero) ~ 95 K was found. XRD studies showed the transformation of all the three nominal compositions into 2201 phase with different T_c s.

Keywords. Superconductivity; T_c enhancement; $\text{Tl}_2\text{Ba}_2\text{Cu}_1\text{O}_x$.

1. Introduction

The T_c of calcium-free $\text{Tl}_2\text{Ba}_2\text{CuO}_x$ compounds studied by various groups (Perkin *et al* 1988; Shimakawa *et al* 1988; Sheng and Hermann 1988; Kondoh *et al* 1988; Torardi *et al* 1988) shows that it ranges from zero to an onset temperature of 90 K. The observation of lower T_c in calcium-free members of $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$ series strongly suggested the importance of Ca in these compounds and also in Bi-based superconducting series. It has also been theoretically predicted (Wheatley *et al* 1988) that the variation of n (i.e. the number of CuO_2 layers) depends upon the number of Ca atoms in the lattice and that Ca gives a stability to the lattice with an enlarged parameter (c) up to 37 Å having extra CuO_2 layers. However, Torardi *et al* (1988) stated that the reported experimental conditions viz the nominal composition of Tl–Ba–Cu–O (2201), the sintering temperature of 850 – 950°C and the sintering time of 5 to 45 min only occasionally result in a T_c of 90 K (onset). Generally the T_c is less than 25 K and special quenching at liquid nitrogen gives a T_c of 55 K while normal cooling results in a non-superconducting state. Experiments with Cu-rich nominal composition (2202) show T_c s up to 70 K (Shimakawa *et al* 1989). In this paper, we report the observation of a T_c (onset) of 115 K and a T_c (zero) of 95 K in calcium-free 2201 phase and the different fabrication approaches resulting in 2201 compounds with T_c s higher than the previously reported onset of 90 K.

2. Experimental

Samples of different compositions of the series $\text{Tl}_m\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$ with starting compositions 2201, 1201 and 2202 were made by solid-state reaction taking appropriate quantities of Ba, Cu and Tl oxides. Two different approaches were used to obtain these oxides viz (i) precipitation method and (ii) taking specpure oxides of Ba, Cu and Tl. In the precipitation method, a solution containing highly soluble metal salt such as chlorides of Ba and Cu was mixed with a solution containing the precipitating agent such as oxalic acid and sodium hydroxide. When the solutions were thoroughly

mixed, an insoluble precipitate was formed. After filtering this precipitate and ensuring that no alkali was present was heated to 300°C for 5–6 h and then at $850\text{--}900^{\circ}\text{C}$ for 6 h with intermittent grindings. Appropriate quantities of Ti_2O_3 prepared from thallos sulphate were then mixed with Ba and Cu oxides, ground thoroughly and after pelletization the composition was sintered at $970 \pm 5^{\circ}\text{C}$ for different durations in a constant flow of oxygen. In the second approach, oxides of Ba and Cu were taken in appropriate amounts required for nominal composition, were ground and the mixture kept in the furnace for 5–6 h at $850\text{--}870^{\circ}\text{C}$. This powder was again ground and pelletized and heated at 910°C for 6 h. These pellets of Ba and Cu oxides were ground and the required amount of Ti_2O_3 was mixed. This mixture was made homogeneous and pellets of 1 cm diameter and 0.2 cm thickness were made. These pellets were then sintered at $970 \pm 5^{\circ}\text{C}$ for different durations. A number of pellets were made and different combinations of nominal composition, sintering temperature and duration were tried. It was found that near the melting temperature of 970°C different compositions showed different types of behaviour. The parameters were then optimized and furnace cooling was found to be suitable after flash sintering. Quenching at room temperature or at liquid nitrogen showed low T_c (zero) or non-superconducting behaviour.

T_c was determined by resistivity measurements using the four-probe a.c. method for 300 K to 70 K. XRD patterns were taken using standard Cu– K_α radiation on a Siemens D-500 diffractometer.

3. Results and discussion

The following is an outcome of the number of experimentations starting from different nominal compositions (2201, 1201, 2202 etc.) to realize the high T_c phase. As shown in figure 1a, the starting composition 2201 did not get converted into a high T_c phase and

Figure 1a. Resistance versus temperature behaviour of TlBaCuO transforming into 2201 phase. (A) 1201, (B) 2201, (C) 2202, (D) the reported highest T_c of 2201 phase.

Figure 1b. Resistance versus temperature behaviour of nominal composition 2202 transforming into 2201 phase with different sintering times: (A) 5 min, (B) 7 min, (C) 10 min, (D) 15 min.

after optimization a broad resistivity drop with an onset T_c of 97 K was observed (table 1). XRD studies (figure 2) show a distorted 2201 phase along with un-reacted Tl_2O_3 and $BaCuO_2$ phase. The low angle XRD pattern, which details the c -parameter, shows a peak at 7.75 degrees and the lattice parameter of this phase was found to be $a \sim 3.86$ Å and $c \sim 23.23$ Å. In the same optimized conditions of sintering the starting composition 1201 ($Tl_1Ba_2Cu_1O_x$) shows formation of enhanced T_c phases with onsets of 86.4 K and 97.2 K when sintered for 2 and $3\frac{1}{2}$ min respectively (see figure 1a, b and table 1). The XRD pattern of samples of 1201 nominal composition is compatible with a well-defined structure of 2201 phase having a low angle peak at 7.6° and a c -axis of ~ 23.23 Å. This suggests that the 1201 is transformed into 2201, i.e. $Tl_2Ba_2CuO_x$ compound (figure 3). The intermediate compositions (1.5, 201) $Tl_{1.5}Ba_2CuO_x$ did not yield any superconductivity at all.

The highest T_c in 2201 compound was observed when the starting composition $Tl_2Ba_2Cu_2O_x$ (2202) was converted into the 2201 phase. The optimized sintering temperature of $975 \pm 5^\circ\text{C}$ and sintering duration of 5–15 min gave a T_c (onset) of 115 K and T_c (zero) of 95.1 K (figure 1), which is higher by 10 K than any of the previous reports and is at par with the next member of the series having two CuO_2 layers with one Ca plane. XRD studies of samples of 2202 nominal composition showed various peaks (figure 4) which can be indexed with $a \sim 3.86$ Å and $c \sim 23.2$ Å. The whole pattern suggests the formation of 2201 with unreacted Tl_2O_3 , CuO and $BaCuO_2$ phases. The low angle peak at $2\theta \sim 7.7$ degrees supports the same contention.

Table 1.

Sample	Sintering time (min)	T_c (K)	T_c^{on} (K)	Remarks
Nominal composition $\text{Tl}_2\text{Ba}_2\text{Cu}_1\text{O}_x$	2	—	—	No resistance drop only metallic down to 70 K. No 2201 phase
Final composition $\text{Tl}_2\text{Ba}_2\text{Cu}_1\text{O}_x$	5	< 70	97.2	No superconducting transition down to 70 K, broad resistivity drop: Highly distorted 2201 phase formation
Nominal composition $\text{Tl}_2\text{Ba}_2\text{Cu}_1\text{O}_x$	2	79.2	97.2	Major phase formed: 2201
$\text{Tl}_2\text{Ba}_2\text{Cu}_1\text{O}_x$	$3\frac{1}{2}$	86.4	97.2	
Final composition $\text{Tl}_2\text{Ba}_2\text{Cu}_1\text{O}_x$	5	< 70	89.8	Distorted 2201 phase with other phases
$\text{Tl}_2\text{Ba}_2\text{Cu}_1\text{O}_x$	10	—	—	No superconductivity
Nominal composition $\text{Tl}_2\text{Ba}_2\text{Cu}_1\text{O}_x$	2	—	—	No resistivity drop down to 70 K; only metallic behaviour with no 2201 phase
$\text{Tl}_2\text{Ba}_2\text{Cu}_1\text{O}_x$	$3\frac{1}{2}$	—	—	
Final composition $\text{Tl}_2\text{Ba}_2\text{Cu}_1\text{O}_x$	5	95.1	115.0	2201 is the dominant phase observed in XRD (for resistivity data see figure 1b)
$\text{Tl}_2\text{Ba}_2\text{Cu}_1\text{O}_x$	7	90.2	104.0	
	10	85.0	100.0	
	15	81.5	115.5

Figure 2. XRD pattern of nominal composition 2201 showing a distorted 2201 phase formation.

From the above studies one can conclude that the high T_c up to 115 K (onset) and 95.1 K (zero) 2201 phase can be formed from three different nominal compositions 2201, 1201 and 2202, when sintered at $975 \pm 5^\circ\text{C}$ for optimized durations. XRD studies of all the compositions show $a \sim 3.86 \text{ \AA}$ and $c \sim 23.23 \text{ \AA}$. The c -axis equal to 23.23 Å suggests that the phase formed is not 2212 which should have $c \sim 29 \text{ \AA}$. The enhanced T_c is due to 2201 phase and the possibility of Ba or any other impurity atom occupying

Figure 3. XRD pattern of nominal composition 1201 showing a well-defined 2201 phase.

Figure 4. XRD pattern of nominal composition 2202 showing formation of 2201 phase.

Ca site is remote. This indicates that the role of CuO_2 layers and Ca atoms as the T_c controlling parameters needs further investigation. Detailed studies are in progress.

References

- Kondoh S, Ando Y, Onoda M, Sato M and Akimitsu J 1988 *Solid State Commun.* **65** 1329
 Perkin S S P, Lee V Y, Nazzari A I, Savoy R, Huang T C, Gorman G and Bayer R 1988 *Phys. Rev.* **B38** 6531
 Sheng Z Z and Hermann A M 1988 *Nature (London)* **332** 55
 Shimakawa Y, Kubo Y, Manako T, Nakabayashi Y and Igarashi H 1988 *Physica* **C156** 97
 Shimakawa Y, Kubo Y, Manako T, Satoh T, Iijima S, Ichihashi T and Igarashi H 1989 *Physica* **C157** 279
 Torardi C C, Subramani M A, Calabrese J C, Gopalakrishnan J, McCarron M, Marrissey K J, Askew T R, Flippin R D, Chowdhry U and Sleight A W 1988 *Phys. Rev.* **B38** 225
 Wheatley J M, Hsu T C and Anderson P W 1988 *Nature (London)* **333** 121