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1990 J. Phys.: Condens. Matter 2 6083

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LETTER TO THE EDITOR

The preparation of an enhanced- T_c superconducting $\text{Tl}_2\text{Ba}_2\text{CuO}_x$ phase by using low Tl concentrations

K K Saini, C P Sharma, S N Ekbote, D K Suri, Pavas Asthana,
Chanderkant, K C Nagpal, S A Agnihotry and Subhas Chandra
National Physical Laboratory, Dr K S Krishnan Road, New Delhi 110012, India

Received 3 November 1989

Abstract. Calcium-free high- T_c superconducting compounds of the $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$ series have been fabricated with an enhanced onset critical temperature, $T_c^{\text{on}} \approx 97.2$ K. The optimisation of parameters has revealed that the choice of nominal composition plays an important role in the formation of the final phase. While a nominal 2201 composition did not yield a high- T_c phase, compounds with low thallium concentration (1201) gave a 2201 high- T_c phase. XRD studies confirm the formation of a 2201 phase from 1201 and $\frac{1}{2}$ 201 phases with $a \approx 3.86$ Å and $c \approx 23.23$ Å. It has also been found that a high sintering temperature of 970 °C maintained for a short duration of three to five minutes is favourable for the enhancement of T_c .

The thallium-based copper oxide superconducting systems of the $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$ series have attracted a great deal of attention recently, because of their high T_c of 125 K. Expectations of an even higher T_c —up to 140 K—have prompted a flurry of activity, manifesting itself in several reports on systems with varied composition and fabrication conditions [1–5].

The importance of the copper oxide layer in enhancing T_c has been recognised in Tl mono- and bi-layer compounds [1] and it has been generally accepted that the increase in the number of CuO_2 layers produced by adding Ca (cation) planes can improve T_c [6] although the maximum T_c of mono-layer compounds is always lower than that of the bi-layer Tl-based superconductors. The highest reported value of T_c for mono-layer Tl compounds ($\text{Tl}_1\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$) is 110 K for 1223 material, i.e. for $n = 3$, and that for bi-layer compounds (2223) is 125 K, again for the $n = 3$ composition. Further enhancement of T_c with $n = 4$ and $n = 5$ is expected but has not been realised yet. Although some results showing a decrease of T_c with increase in n have appeared, confirmation is still awaited. The role of calcium (cation) planes seems evident, as they lie within the interior of Cu perovskite-like units, and observation of relatively low T_c values in calcium-free compounds (1202, 2201) strongly supports the above criterion; but the range of observed T_c —which is from non-existent (no superconductivity) to 20 K in 1201, and 0–90 K in 2201—makes the problem more perplexing and interesting. This is especially so for 2201 compounds when the onset T_c of the next member of the series, $n = 2$ (2212) ($\text{Tl}_2\text{Ba}_2\text{Ca}_1\text{Cu}_2\text{O}$), ranges from 95 to 108 K [4]. Generally the observed T_c of the 2201 phase is 15–20 K and recently, in samples quenched in liquid nitrogen, T_c

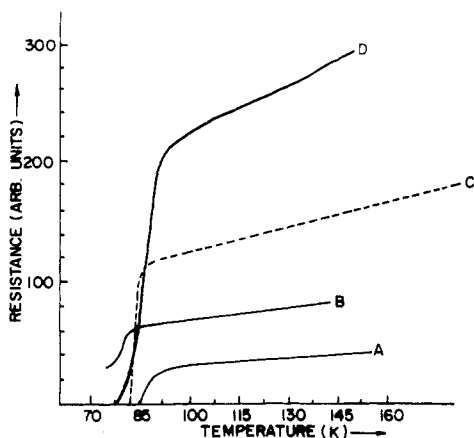


Figure 1. Temperature versus resistance curves for the final 2201 phase obtained starting from different nominal compositions: (A) $\text{Tl}_1\text{Ba}_2\text{CuO}_x$; (B) $\text{Tl}_2\text{Ba}_2\text{CuO}_x$; (C) $\text{Tl}_2\text{Ba}_2\text{CuO}_x$ reported on previously [5]; (D) $\text{Tl}_{0.5}\text{Ba}_2\text{CuO}_x$.

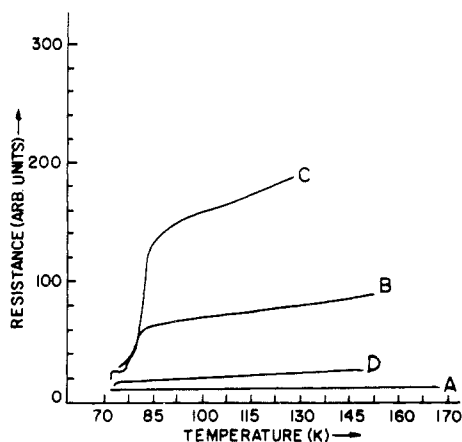


Figure 2. Temperature versus resistance curves for $\text{Tl}_2\text{Ba}_2\text{CuO}_x$ (nominal composition) for different sintering durations: (A) 2 min; (B) = 3.5 min; (C) 5 min; (D) 10 min.

has gone up to 50 K [7]. Values of T_c^{on} of 90 K and T_c^0 of 83 K are relatively difficult to observe for the reported conditions.

In this paper we report on the high-temperature sintering of different nominal compositions of $\text{Tl}_m\text{Ba}_2\text{Cu}_2\text{O}_x$ ($m = 1, 2$) with different sintering times and compositions, which resulted in the formation of compounds with an enhanced T_c^{on} of 97.2 K and T_c^0 of 86.2 K, repeatedly. In this observation, T_c is nearly 7 K higher than in any previous report (figure 1) and is on a par with the T_c of the $n = 2$ (i.e. with one calcium plane) material, suggesting that it is not just the presence of Ca that takes a role in enhancing T_c .

Samples were prepared by the solid state reaction method, using appropriate amounts of highly pure (Specpure 99.99%) oxides of Ba, Cu and Tl. Investigations of two different series were performed in which the nominal compositions of $\text{Tl}_2\text{Ba}_2\text{CuO}_x$ and those with low concentrations of Tl ($\text{Tl}_{0.5}\text{Ba}_2\text{Cu}_1\text{O}_x$ and $\text{Tl}_1\text{Ba}_2\text{CuO}_x$) were studied extensively, and which have resulted in the high- T_c phase 2201. Some compounds with intermediate concentrations of Tl not yielding the high- T_c phase were also prepared.

The method of preparation was the same for all series, and is as follows. First, BaO and CuO powders were mixed and ground, and the mixture was kept in the furnace for 5–6 h at temperatures between 850 and 870 °C. The powder was then ground and pelletised and the pellets were further heated at 910 °C for 6 h. These pellets were again ground and mixed with the appropriate amount of Tl_2O_3 . This mixture was thoroughly mixed and made into pellets 1 cm in diameter and about 2 mm thick. These pellets were sintered at 970 °C for different time periods (see table 1). A number of pellets were made and sintered at different temperatures in a closed ceramic crucible in a constant flow of oxygen. After this process the temperature of 970 °C, which is close to the melting point, was found to be optimum. It was found that sintering times of less than 3 min and more than 10 min do not yield the desired results. The optimal time lies between three and four minutes. Furnace cooling was found suitable for most samples and some quenching experiments were also done. It was found that quenching in liquid nitrogen

Table 1. The effects of altering the sintering times for different compositions.

Sample number	Sample	Sintering time (min)	T_c^0 (K)	T_c^{on} (K)	Remarks
1	The nominal composition $\text{Tl}_{0.5}\text{Ba}_2\text{CuO}_x$	2	—	77 93	Two resistivity drops XRD shows the distorted 2201 phase with unreacted Tl_2O_3 etc
	Final composition $\text{Tl}_2\text{Ba}_2\text{CuO}_x$	$3\frac{1}{2}$	77	93	XRD pattern shows the distorted 2201 phase with Tl_2O_3 unreacted
2	The nominal composition $\text{Tl}_1\text{Ba}_2\text{Cu}_1\text{O}_x$	2	79.2	97.2	} The major phase formed is 2201
		$3\frac{1}{2}$	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
3	The nominal composition $\text{Tl}_2\text{Ba}_2\text{Cu}_1\text{O}_x$	2	—	—	No resistance drop; only metallic 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

gives a non-superconducting sample, while air quenching results in the formation of a low- T_c phase.

Measurements of T_c were made by measuring the resistivity by a four-probe AC method from 300 K to 70 K. X-ray diffraction (XRD) patterns were taken using the standard Cu $K\alpha$ radiation with a Siemens D-500 diffractometer.

Figure 2 shows the resistivity curves of compounds formed using the nominal composition 2201 with different sintering times. It is seen that allowing a comparatively short sintering period of 2 min does not yield superconductivity at all, and allowing a long sintering period of 15–20 min results in either the melting of the sample or the material becoming non-superconducting. The optimal sintering time is 3–5 min at 970 °C, which yields the 2201 phase with a small drop at 77 K, but not complete superconductivity (table 1). It was repeatedly observed that if the starting composition is 2201 the final product is generally not the 2201 phase, and also that T_c is low. Parkin *et al* [8, 9] have reported that the 1323 composition gives 2223 as the predominant superconducting phase. Keeping this in mind, we experimented with three concentrations of Tl: $\text{Tl}_{0.5}$ ($\frac{1}{2}$ 201), Tl_1 (1201) and $\text{Tl}_{1.5}$ ($1\frac{1}{2}$ 201), and as shown in figure 3 found that for optimised sintering conditions, i.e. a sintering time of 3.5 min at 970 °C, the nominal composition $\text{Tl}_{0.5}\text{Ba}_2\text{Cu}_{1.5}\text{O}_x$ gave rise to a 2201 phase with $T_c^{\text{on}} \approx 97$ K and $T_c^0 \approx 77$ K. The small knee of the resistivity curve suggests the formation of two phases. For the lower sintering period of two minutes, although no region of zero resistance has been found down to 70 K, two drops in the resistivity curve are evident, one at ≈ 77 K and the other at ≈ 95 K. The superconductivity is destroyed for longer sintering periods of 5 and 10 min under the same conditions of preparation. The nominal composition 1201 transformed into the 2201 phase showed $T_c^{\text{on}} \approx 97.2$ K and $T_c^0 = 86.4$ K (figure 4). For a relatively small sintering time, i.e. 2 min at 970 °C, a T_c^{on} of 97.2 K and T_c^0 of 79.2 K were observed. Sintering for shorter durations does not result in the formation of a superconductor. When the sintering time was increased, i.e. to 5–10 min, a low- T_c 2201 phase was obtained, but it has been repeatedly observed that the nominal composition 1201,

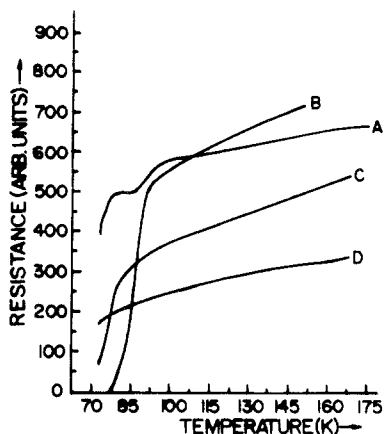


Figure 3. Temperature versus resistance curves of $Tl_{0.5}Ba_2CuO_x$ (nominal composition) for different sintering durations: (A) 2 min; (B) \approx 3.5 min; (C) 5 min; (D) 10 min.

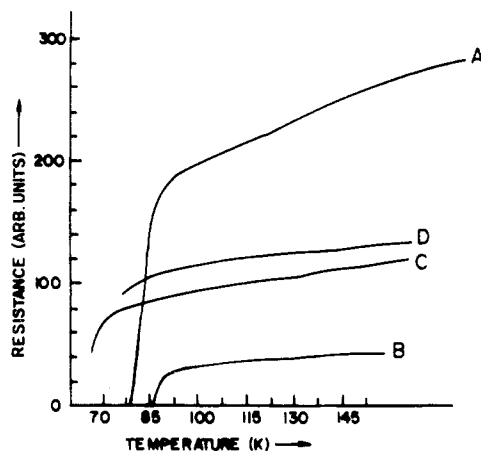


Figure 4. Temperature versus resistance curves for the $Tl_1Ba_2CuO_x$ nominal composition for different sintering durations: (A) 2 min; (B) \approx 3.5 min; (C) 5 min; (D) 10 min.

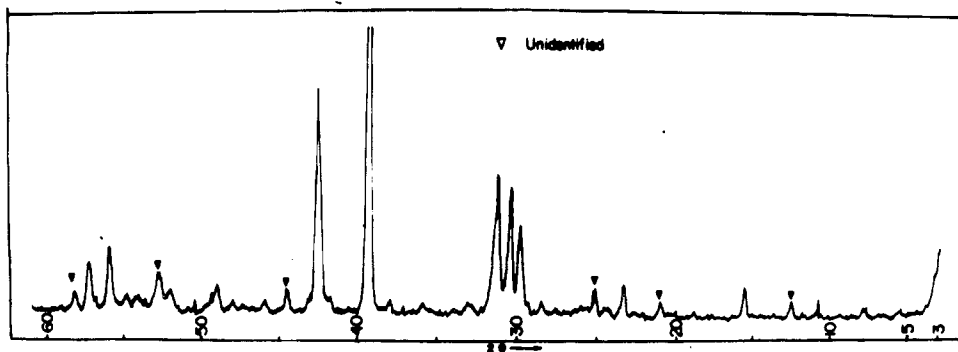


Figure 5. The XRD pattern of $Tl_1Ba_2CuO_x$ (nominal composition) showing the formation of the distorted 2201 phase and unreacted Tl_2O_3 and $BaCuO_2$ phases.

sintered at 970 °C for 3–4 min in a constant flow of oxygen, results in a 2201 phase with a T_c^{on} of 97.2 K. The XRD studies of 2201 (obtained from 2201, $\frac{1}{2}$ 201 and 1201 nominal compositions) are shown in figures 5, 6 and 7. It is interesting that the distorted 2201 phase shows two peaks on the low-angle side ($2\theta \approx 7.6^\circ$ and 7.9°) suggesting that the 2201 phase has two different values of the parameter c (figure 5). It contains some Tl_2O_3 and $BaCuO_2$, and showed some distortion in the lattice also. The XRD pattern of sintered $Tl_{0.5}Ba_2CuO_x$, nominal composition $\frac{1}{2}$ 201, is shown in figure 6. The lattice parameters, from the indexing of the observed peaks, are $a \approx 3.84 \text{ \AA}$ and $c \approx 22.87 \text{ \AA}$ and the low-angle peak is at $2\theta \approx 7.8^\circ$ which indicates the formation of the 2201 phase. These observations also support the above contention—i.e. that the 2201 phase is formed from the low-Tl-concentration nominal composition ($\frac{1}{2}$ 201). In the case of the 2201 phase obtained from the 1201 nominal composition, the zero resistance, and sharp XRD, as shown in figure 7, clearly indicate the major phase with $a \approx 3.86 \text{ \AA}$ and $c \approx 23.23 \text{ \AA}$. The high value of c (23.23 \AA) for this composition suggests a higher T_c than in previous

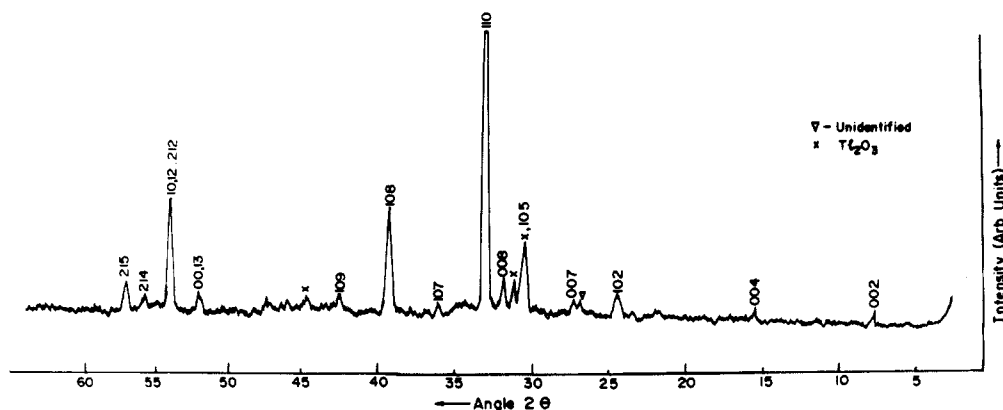


Figure 6. The XRD pattern of $Tl_{0.5}Ba_2CuO_x$ (nominal composition). Formation of the 2201 phase is evident and some unreacted Tl_2O_3 is also present.

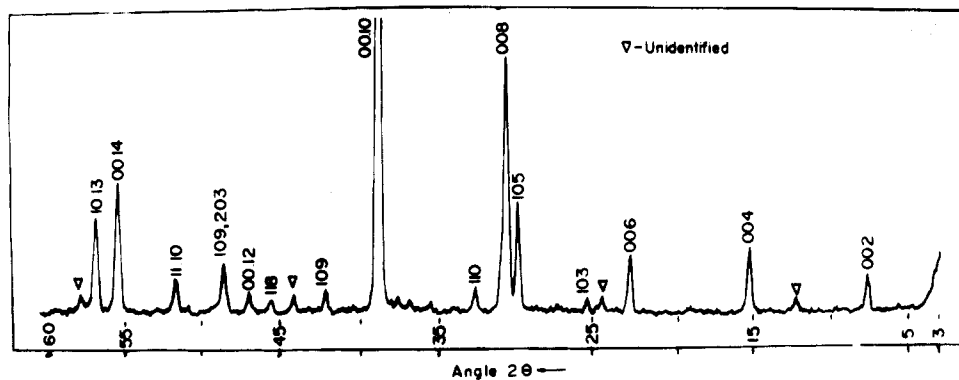


Figure 7. The XRD pattern of $Tl_1Ba_2CuO_x$ (nominal composition). This shows the formation of the 2201 major phase and some unreacted Tl_2O_3 .

reports, where $c \approx 23.12 \text{ \AA}$, and the transformation is of Tl_1 into Tl_2 . Furthermore, from the 7.6 peak one may conclude that although the T_c is equivalent to that of the $n = 2$ ($Tl_2Ba_2CaCu_2O_x$) phase, the structure is only 2201 and the possibility of some other atom, e.g. Ba, occupying the Ca site seems to be negligible.

In conclusion, we have observed an enhanced T_c of 97.2 K for the 2201 phase after sintering at a high temperature of 970 °C. The relatively short durations of sintering (2–5 min) give favourable results with the low-Tl-concentration starting compositions 1201 and $\frac{1}{2}$ 201. The nominal composition 2201 does not give a high- T_c 2201 phase. XRD studies of the 2201 phase prepared from 1201 and $\frac{1}{2}$ 201 phases revealed that although the T_c is on a par with that of the 2212 phase, the low-angle diffraction peaks are at $2\theta \approx 7.7^\circ$, which suggests that there seems to be no occupation of Ca sites by Ba or other atoms.

This result may be important in the context of the role of Ca layers and vacancies of Ca [10] for the enhancement of T_c . It seems that, as suggested previously in [7], the distorted lattice improves the T_c of Tl-based superconductors.

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