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Synthesis of single phase Tl-2223 superconductors: How much thallium do we really need?

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Abstract. This paper describes the synthesis and microwave absorption studies of single phase Tl-2223 compound, with $T_c = (129 \pm 1)$ K. The single phase compound has been synthesized using a precursor matrix method. It has been found that Tl-deficient starting composition gives the best results.

Keywords. High temperature superconductor; Tl-2223 phase; microwave absorption of superconductors.

1. Introduction

The high temperature superconductivity with T_c ($R = 0$) up to 125 K has been established for the homologous series $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+4}$ (Ginley *et al* 1988; Gopalakrishnan *et al* 1988; Hazen *et al* 1988; Zheng and Hermann 1988; Kikuchi *et al* 1989; Parkin *et al* 1988a, b; Torardi *et al* 1988) with the underlying superconducting phase $Tl_2Ca_2Ba_2Cu_3O_{10}$ designated as Tl-2223 phase. In these compounds the superconducting phases $Tl_2CaBa_2Cu_2O_8$ (with $T_c = 108$ K designated as Tl-2122) and Tl-2223 phases have been studied extensively and their structural analysis suggests ~ 10–15% vacancies at Tl sites (Hewat *et al* 1988; Cox *et al* 1988; Otto *et al* 1988; Sequeira *et al* 1988; Syono *et al* 1989; Zetterer *et al* 1988). It has been argued by us in an earlier communication (Sequeira *et al* 1988) that the Tl double layers cannot possibly sustain full Tl occupancy due to excess positive charge and in the case of Tl-2122 we could in fact successfully substitute K^+ ions at $\sim 50\%$ of the Tl-sites and synthesize $Tl_1K_1Ca_1Ba_2Cu_2O_x$ without any significant deterioration in the superconducting behaviour (Iyer *et al* 1988; Sequeira *et al* 1988). This raises doubts whether all the stoichiometric amount of thallium i.e. two thallium atoms per formula are really needed to stabilize the Tl double layers in Tl-2122 and Tl-2223 phases. Eibschutz *et al* (1988) reported a superconducting phase with zero resistance temperature of 121 K from a starting composition $Tl_{0.5}Ca_2Ba_2Cu_3O_x$. The underlying superconducting phase in this compound should be none other than Tl-2223 since the single layer Tl-1223 phase is known to have $T_c(R = 0)$ not exceeding 110 K (Haldar *et al* 1988; Parkin *et al* 1988a).

In this paper, we report the synthesis of single-phase superconducting compounds in Tl-Ca-Ba-Cu-O system from a number of different nominal compositions mostly Tl-deficient and have identified the phase to be Tl-2223 and arrived at the optimum (Tl + Ca) composition which yields the single-phase 2223 compound.

2. Synthesis of the Tl-based superconductors

The conventional solid state reaction route namely mixing and heating of the constituent oxides Tl_2O_3,CaO,BaO and CuO has not been found to be effective due to

the high volatility and low melting point of Tl_2O_3. At the reaction temperatures at which the compound is expected to be formed, Tl_2O_3 was found to be lost even before the reaction was complete. To avoid this, the Tl-2223 phase has been synthesized in this work using a precursor matrix method—with the precursor of composition $Ca_qBa_2Cu_nO_x (2 < q < 3.0$ and $n = 2, 3)$ heating with Tl_2O_3 at high temperature for a short time.

The required matrix has been synthesized by heating a mixture of $BaCO_3$, $CaCO_3$ and CuO in the required proportions at 700°C for 20 hr, followed by heating at 850°C for 48 hr and the final heating at 930°C for 120 hr under flow of oxygen, with several intermittent grindings and pelletization. Subsequently Tl_2O_3 and the matrix $Ca_qBa_2Cu_3O_x$ have been thoroughly mixed in the required proportions to give a nominal composition $Tl_pCa_qBa_2Cu_3O_x$, pelletized into discs with 12 mm dia (1 g) and wrapped in nickel foil to reduce thallium losses during heat treatment. The pellets were introduced in a preheated furnace at 900–960 °C for varying times (20–40 min) followed by quenching to room temperature by withdrawing from the furnace. The quenched pellet was annealed in oxygen by reintroducing it in a preheated furnace (900–960°C) and furnace-cooled under oxygen by putting off the furnace. The surface of the pellets in many cases showed higher room temperature resistance which was reduced to milliohms on scrapping the surface. This may be attributed to the contamination with nickel foil. The formation of the compound has been found to be associated with simultaneous increase in volume of the pellet. The preparation conditions are summarized in table 1. The flow diagram for the synthesis is shown schematically in figure 1.

The X-ray diffraction patterns were recorded for all the samples with Ni-filtered Cu-Kα radiation on a Philips PW 1050 wide angle goniometer. For the samples reported in tables 1 and 2 the lines characteristic of the respective precursor matrix were found to be completely absent thus confirming its complete reaction with Tl_2O_3. Typical X-ray diffraction patterns for matrix $Ca_2Ba_2Cu_3O_x$ and $Tl_{1.25}Ca_2Ba_2Cu_3O_x$ are given in figures 2A and 2B.

3. EPR and electrical resistivity measurements

We have shown earlier (Sastry *et al* 1988) that EPR-spectrometric measurements can be effectively used to detect the superconducting phase, even in powder samples, by following the temperature dependance of microwave reflectivity/absorption from a resonant cavity loaded with the superconducting sample. This technique has been extensively used in this study as a first-level evaluation of the quality of superconductors synthesized from different compositions. A Varian V 4502 X-band ESR spectrometer equipped with a closed cycle helium refrigerator has been used in the temperature range 20 K to 300 K. Electrical resistivity measurements have been carried out between 77 K and 300 K using a DC four-probe method with a measuring current of 1 mA. It has been demonstrated in our laboratory earlier that the microwave absorption shows a sharp drop at a temperature where the electrical resistance of cuprate superconductors becomes zero.

Chemical analysis conducted on these samples confirmed that the stoichiometry of the product was close to the starting compositions and the Tl-content was not altered to any measurable extent during synthesis.

$$qCaCO_3 + 2BaCO_3 + 3CuO \longrightarrow Ca_qBa_2Cu_3O_x$$
$$Ca_qBa_2Cu_3O_x + pTl_2O_3 \longrightarrow Tl_pCa_qBa_2Cu_3O_x$$
$$2 < q < 3,\ 0.5 < p < 1.25$$

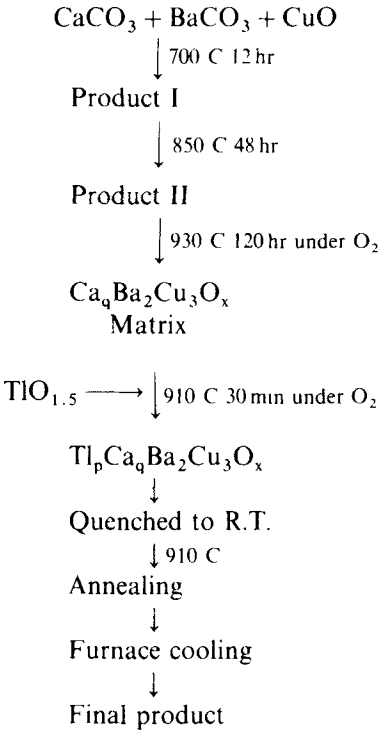

Figure 1. Synthesis of Tl-2223 single phase compound matrix reaction method.

Table 1. Preparation conditions and synthesized products from $Tl_1Ca_2Ba_2Cu_3O_x$ as starting nominal composition: Effect of temperature and heating time duration.

Temperature (C)	Heating time (min)	Products	$T_c(R=0)(\pm 1\ K)$
900	30	2122 + 2223	Mixed phase compound
905	30	2223(2122 impurity)	123
910	20	2223	123
	30	2223	129
	40	2223	127
915	30	2223	127
920	30	2223(2122 impurity)	125
930	30	Compound melts with partial decomposition	115
940	30	Compound melts with decomposition	
960	20	-do-	

Table 2. Synthesis of Tl-2223 from Tl-deficient nominal compositions: Effect of calcium and thallium concentration on T_c ($R = 0$)

Nominal composition	Phase formed	T_c ($R = 0$)	(Tl + Ca)
$Tl_{0.5}Ca_3Ba_2Cu_3O_x$	2223	130	3.50
$TlCa_2Ba_2Cu_3O_x$	2223	130	3.00
$Tl_{1.25}Ca_2Ba_2Cu_3O_x$	2223	121	3.25
$Tl_3Ca_2Ba_2Cu_3O_x$	2223	115	5.00
	2122		
$TlCa_{2.25}Ba_2Cu_3O_x$	2223	123	3.25
$TlCa_{2.5}Ba_2Cu_3O_x$	2223	120	3.50
$TlCa_3Ba_2Cu_3O_x$	2223	118	4.00
$Tl_{1.25}Ca_{2.25}Ba_2Cu_3O_x$	2223	116	3.50

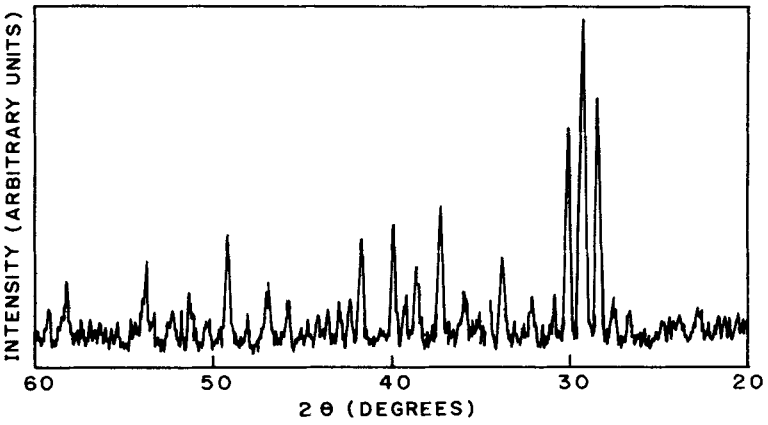

Figure 2A. X-ray diffraction pattern of precursor matrix $Ca_2Ba_2Cu_3O_x$.

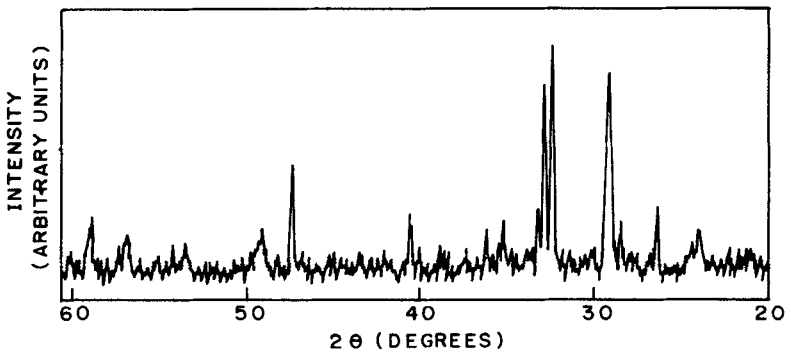

Figure 2B. X-ray diffraction pattern of $Tl_{1.25}Ca_2Ba_2Cu_3O_x$. The absence of precursor matrix lines may be noted.

4. Results and discussion

The results of the phase analysis using X-ray powder diffraction technique and the superconducting transition temperatures from microwave and electrical resistivity measurements for a number of compounds synthesized under different and identical heat treatment protocol as described above from a variety of starting compositions are described in tables 1 and 2, respectively. The microwave data on the compositions listed in table 2 confirmed the presence of only one superconducting transition in each case for samples 1 to 8 except for sample 4 which exhibited two transitions. Figure 3 depicts a typical behaviour of microwave reflectivity data as a function of temperature for samples 3 and 4. This clearly shows that the sample with Tl-rich nominal composition $Tl_3Ca_2Ba_2Cu_3O_x$ shows two superconducting transitions whereas the Tl-deficient sample with nominal composition of $Tl_{1.25}Ca_2Ba_2Cu_3O_x$ shows a metallic behaviour in the normal state and exhibits a sharp transition at 121 K, with no evidence of any other superconducting phase down to 20 K. An examination of the data shown in tables 1 and 2 brings out the following important aspects of the present results:

(i) The synthesis of Tl-2223 from identical Tl-deficient nominal starting compositions is strongly affected by the reaction temperature and the temperature zone for the formation of stable Tl-2223 phase is very narrow viz 910–915°C.

(ii) As low as 25% of the stoichiometric requirement of Tl-content (viz. sample 1 in table 2) is adequate to sustain Tl-2223 structure in single phase.

(iii) For wide composition range with the Tl:Ca ratio varying from 0.5:3, 1:2, 1.25:2, 3:2, 1:2.25, 1:2.5, 1:3, 1.25:2.25, (samples 1 to 8 except 4 in table 2) the 2223 structure results with $T_c(R = 0)$ value ranging from 130 K to 116 K, combined stoichiometry of (Tl + Ca) between 3 and 4 invariably leads to the formation of Tl-2223 phase alone.

(iv) At a constant Tl concentration in the starting material, with increase in calcium concentration, T_c $(R = 0)$ value decreases from 130 K to 118 K (table 2, samples 2,5–7) and from 121 K to 116 K (table 2, samples 3 and 8).

(v) At a constant calcium concentration in the starting material, increase in Tl concentration results in the decrease in T_c $(R = 0)$ in 2223 phase and further increase in

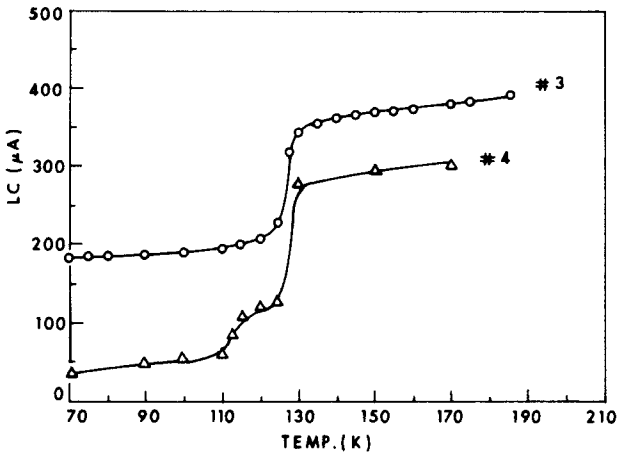

Figure 3. Temperature dependence of microwave absorption (measured as change in leakage currents LC) for samples 3 and 4.

Tl concentration to Tl_3 results in the formation of mixed phase compound with emergence of Tl 2122 phase in the product in significant concentration (table 2, samples 2 to 4).

(vi) The formation of Tl-2223 from nominal thallium-deficient starting compositions e.g. $Tl_1Ca_2Ba_2Cu_3O_x$ is an interesting finding of this investigation. This is probably due to the existence of vacancies at calcium sites which play a crucial role in the formation of pure Tl-2223 phase, the thallium deficiency aiding migration of Ca ions to Tl sites (Iyer *et al* 1989).

5. Conclusions

It is established that using Tl-deficient starting nominal compositions enables one to prepare pure Tl-2223 phase with a T_c $(R=0)$ 129 ± 1 K. Increase in thallium concentration $> Tl_{1.25}$ results in the formation of Tl-2122 as impurity phase. Compositions containing $(Tl + Ca) > 4$ lead to the stabilization of both Tl-2223 and Tl-2122 phases.

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