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# Phase Formation and Grain Growth Kinetics of High- $T_c$ Superconducting Tl-1223 Ceramics

S. Heede<sup>a</sup>, M. Ullrich<sup>b</sup>, H.C. Freyhardt<sup>a,b</sup>, R.E. Gladyshevskii<sup>c</sup>, E. Bellingeri<sup>c</sup>, R. Flükiger<sup>c</sup>

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The phase formation and grain growth of  $(\text{Tl,Pb,Bi})(\text{Sr,Ba})_2\text{Ca}_2\text{Cu}_3\text{O}_{9.8}$  ceramics were investigated in the temperature range between 860°C and 1000°C. It was found that partial melting seems to improve the texture of the samples. The phase purity, however, is limited due to an incomplete re-precipitation process due to the formation of a liquid phase, which is already present above 885°C. The resulting grain growth exponent  $n$ , however, appears to differ from the classical exponent of 1/3 for the coexistence of a liquid phase in the temperature range between 885°C and 920°C. For the first time, the activation energy for the high- $T_c$  Tl-1223 phase has been determined showing faster grain growth kinetics than for Y-123 and Bi-2223.

**KEY WORDS:** Tl-1223, high- $T_c$  superconductors, grain growth kinetics, activation energy

## 1. INTRODUCTION

Significant efforts have been directed towards the development of silver-sheathed Tl-based superconducting wires and tapes.  $(\text{Tl,Pb})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$  (Tl-1223) is an interesting material for some applications. The smaller anisotropy with respect to Tl-2223, due to the presence of a single insulating TlO layer between the current-carrying  $\text{CuO}_2$  layers, is responsible for a more effective flux pinning and the pronounced irreversibility at 77 K [1,2]. This, combined with its high  $T_c$  (110-120 K, [3]) and high intragrain critical current density, gives the superconducting Tl-1223 phase basis for the interest in.

Unfortunately, at 77 K the transport critical current density in magnetic fields, especially of Tl-1223 tapes produced by the powder-in-tube (PIT) technique, is still too low for a wide range of applications. Two main reasons have been shown to be responsible for this behavior. One reason is the phase purity of the samples which could be increased only up to about 90-95 wt.% at present. There is still no consensus on how to optimize the phase purity of Tl-1223. Because of the high volatility of thallium, Tl-1223 powder with a morphology suitable for the fabrication of superconducting Ag-sheathed tapes is not easily obtainable. To compensate the Tl losses, different solutions have been proposed. Some research groups wrap the precursor material in foil to minimize the Tl loss whereas other groups add an excess of Tl to ensure

a complete reaction. Furthermore, it has been found that when Bi is partially substituted for Tl (Pb), and Ba for Sr, the phase purity can be increased to (95wt%) [4]. One has to keep in mind, however, that a specific amount of very small inclusions is necessary for good flux pinning. High-purity  $(\text{Tl,Pb,Bi})(\text{Sr,Ba})_2\text{Ca}_2\text{Cu}_3\text{O}_{9.8}$  powders ( $\approx 95$  wt%,  $T_c \approx 120$ -125K) could be produced by applying hot isostatic pressure (HIP) during the reaction [5,6]. Thus, thallium losses were avoided during the synthesis, allowing a good control of the composition of the samples. The second reason is based on the pronounced weak-link behavior which characterizes the superconducting phase. Low density and poor texture have been proven to limit the transport critical current density when applying the powder-in-tube technique. Many attempts have been made to overcome these problems. Since the grain size in general is relatively small (5-10  $\mu\text{m}$ ), several groups have tried to compensate the poor texture by improving the grain connectivity, i.e. the density of the tapes. Different thermal treatments and pressing steps, however, have been found to restrain the  $j_c$  enhancement by the formation of cracks and sausaging effects. In a few cases, 25 - 50  $\mu\text{m}$  large plate-like grains could be obtained by an in-tape reaction involving partial melting by a solution - re-precipitation process [6]. Morgan *et al.* [7] applied a thermal-gradient method to the formation of Tl-1223, however, no pronounced grain alignment was observed. Liu *et al.* [8] managed to improve the texture of Tl-1223 ceramics by substituting Ba for Sr and partial melting, but the overall texture remained too low for applications.

So one has not been successful in optimizing the formation of Tl-1223 tapes by melt-texturing.

<sup>a</sup> Institut für Metallphysik, Universität Göttingen, Hospitalstr. 3/7, D-37073 Göttingen, Germany

<sup>b</sup> Zentrum für Funktionswerkstoffe gGmbH Göttingen, Windausweg 2, D-37073 Göttingen, Germany

<sup>c</sup> Département de Physique de la Matière Condensée, Université de Genève, 24 quai E. Ansermet, CH-1211 Geneva 4, Switzerland

Keeping this in mind, this was the aim of the investigation to collect more information about the phase formation and grain growth kinetics of Tl-1223.

## 2. Synthesis

Binary oxides,  $(\text{Sr,Ca})\text{CuO}_2$ ,  $(\text{Ca,Sr})_2\text{CuO}_3$  and  $\text{BaCuO}_2$  were used to obtain substituted Tl-1223 phases of nominal compositions  $\text{Tl}_{0.6+y}\text{Pb}_{0.2}\text{Bi}_{0.2}\text{Sr}_{1.8}\text{Ba}_{0.2}\text{Ca}_{2-y}\text{Cu}_3\text{O}_{9.5}$  ( $y = 0, 0.1$ ). These compositions were chosen because of the stabilizing effect of the Bi incorporation [4] mentioned above which also allows shorter processing times. Two compositions were tested; however, no significant differences were observed. The alkaline-earth metal cuprates were prepared by calcination of powder mixtures of high purity Sr, Ca and Ba carbonates with CuO in flowing oxygen at 900–980°C for 48 hours.  $\text{Ti}_2\text{O}_3$ , PbO and  $\text{Bi}_2\text{O}_3$  were added to give the nominal compositions and pellets of the resulting powders were sintered at 940°C for 3h under an oxygen partial pressure of 0.5 bar and 50 bar helium [5]. Besides the Tl-1223 phase, the following secondary phases were detected by X-ray diffractometry (XRD), analytical scanning electron microscopy (SEM) as well as energy dispersive X-ray analysis (EDX):  $(\text{Ca,Sr})_2\text{CuO}_3$ ,  $(\text{Sr,Ca})\text{CuO}_2$ ,  $\text{BaBiO}_3$ , Tl-1212 and  $\text{Ca}_2\text{PbO}_4$ .

## 3. Results and discussion

Particular attention was paid to the preparation of Tl-1223 involving partial melting, in order to improve the grain connectivity. Differential thermal analysis (DTA) was carried out to investigate the phase diagram. Pulverized pellets were placed in a gold tube and heat treated under flowing oxygen using a heating and cooling rate of 1.5°C/min. The data (Fig. 1) reveal at least three distinct endothermic peaks. X-ray diffraction measurements were performed to identify the decomposition products. For this purpose, Tl-1223 powder was placed into a pre-heated furnace, kept for 10 minutes at a constant temperature and subsequently quenched in air. Since the endothermic peak at 923°C could not be identified by this method clear indications of its origin were found by SEM/EDX investigations (see below). Above 945°C decomposition of Tl-1223 takes place. Fig. 2 reveals that above 945°C the amount of secondary phases, especially (Ca,Sr)-cuprates and plumbates, increases with increasing temperature. At 963°C clear indications of Tl-1212 appear, in agreement with the observation that (Ca,Sr)- and Cu-rich phases have precipitated from the original Tl-1223

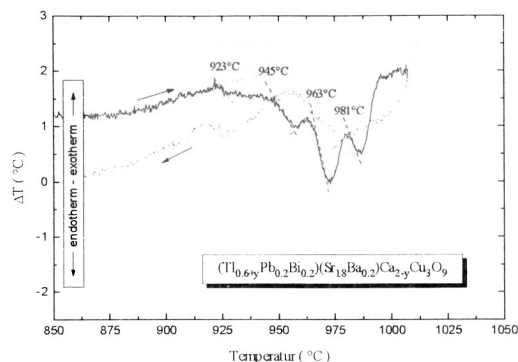


Fig. 1: DTA measurement of Tl-1223 revealing at least three pronounced endothermic peaks. 945°C: decomposition of Tl-1223, 963°C: formation of Tl-1212, 981°C: melting of Tl-1212. The peak at 923°C might be due to the onset of liquid (see below).

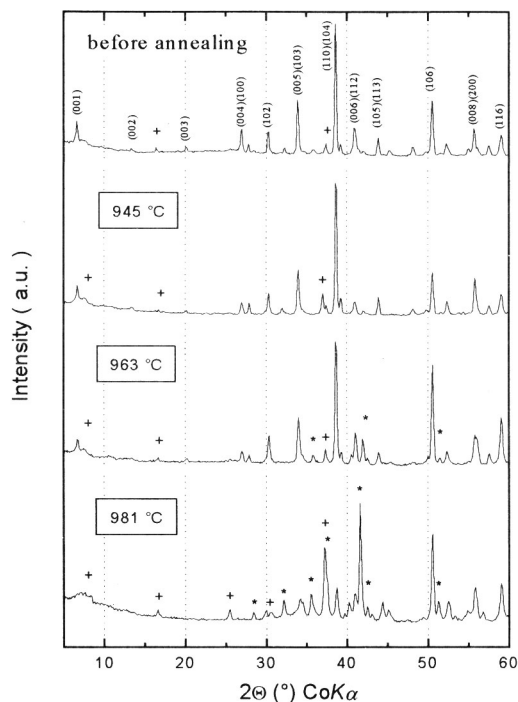


Fig. 2: X-ray diffraction patterns of as prepared samples and samples heat-treated for 10 minutes at 945°C, 963°C and 981°C, corresponding to the DTA measurement. hkl indices of Tl-1223 are indicated on the top diagram. (+) and (\*) denote reflections originating from secondary phases as (Ca,Sr)-cuprates and plumbates and as Tl-1212.

phase. The X-ray diffraction pattern at 981°C indicates that the main phase is Tl-1212, which was also supported by susceptibility measurements made after annealing the powder at 981°C. Scanning electron microscopy provided evidence for the occurrence of melting of Tl-1212 at 981°C.

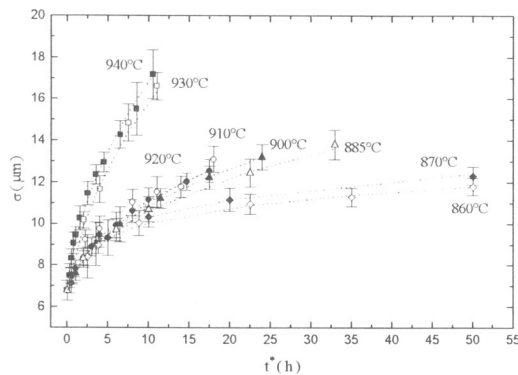


Fig. 3: Average grain size versus annealing time at different temperatures for the composition  $(\text{Tl}_{0.6}\text{Pb}_{0.2}\text{Bi}_{0.2})(\text{Sr}_{1.8}\text{Ba}_{0.2})\text{Ca}_2\text{Cu}_3\text{O}_x$ .

The phase formation was not only investigated with respect to temperature but also as a function of time. Since the DTA revealed a decomposition-onset at 945°C we investigated the phase formation below this temperature.

Basic information about a material's microstructural development can be obtained by studying the grain size with respect to temperature and time. The grain growth kinetics during thermal treatment of polycrystalline Tl-1223 in flowing oxygen was examined by measuring grain sizes by SEM at various times and temperatures between 860 and 940°C. Fig. 3 indicates that the average grain size increases with temperature as well as with time. The standard deviation of the grain size distribution slightly increases with temperature, but remains almost constant with time for each temperature below 940°C. Furthermore, the plate-like shape of the grains, as observed by SEM, becomes more evident with time and temperature.

An interesting feature is the exponential temperature dependence of the annealing time at which a solidified liquid is first observed in the quenched samples (Fig. 4 and Fig. 5) for annealing temperatures above 885°C. No liquid was found below 885°C for times up to 50 h (limits of measurements). Other groups have reported onsets of partial melting for similar Tl-based compositions, like  $(\text{Tl}_{0.5}\text{Pb}_{0.5})(\text{Sr}_{1.6}\text{Ba}_{0.4})\text{Ca}_2\text{Cu}_3\text{O}_x$  at 877°C in air [7] or  $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  at 905°C in oxygen [9], which are in the same temperature range. This result seems to be in disagreement with our DTA measurement, which indicated the onset of peritectic/eutectic melting at 923°C. The onset temperature as determined from SEM studies can be considered to be more reliable since, in

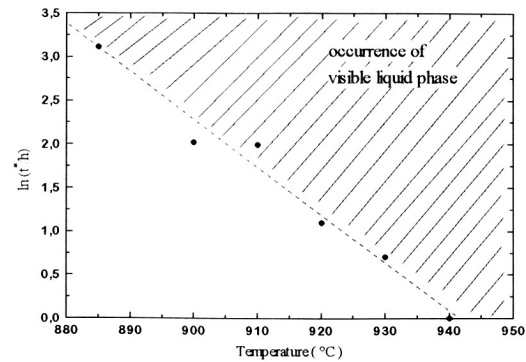


Fig. 4: Annealing time at which a visible liquid phase could be detected ( $\ln t^*$ ) versus annealing temperature.

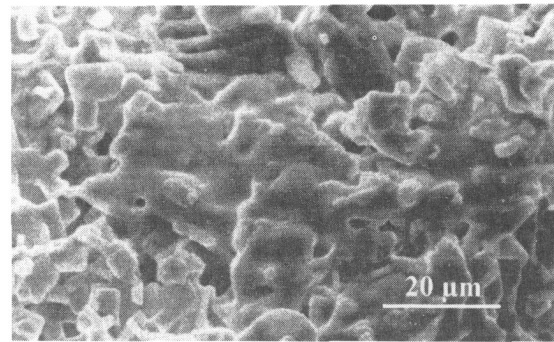


Fig. 5: SEM image revealing the occurrence of a liquid phase between Tl-1223 crystallites.

generell, DTA measurements have shown to slightly depend on the heating rate, the crucible material etc.. Furthermore, common DTA equipments, which use very small amounts of sample, are unable to detect the formation of small quantities of liquid [10].

The presence of a liquid is known to accelerate grain growth as well as to enhance texturing. Beside this, liquid/solid interactions may improve the grain connectivity via a partial extraction of peritectic/eutectic liquid. Ceramics annealed for instance for 1 h at 940°C consisted of small textured domains (Fig. 6). The size of the crystallites exceeded 20 μm which is unusual for Tl-1223. The melt-texturing method as carried out here without a temperature gradient favours a non-directional process so that differently textured domains hinder themselves in developing large uniformly textured domains. This is the reason for the small size of the textured domains depicted in Fig. 6. According to our investigations described above, a liquid is present under these conditions. In contrast to other HTSC materials, however, the grain growth, for the composition investigated above 885°C, is always accompanied by

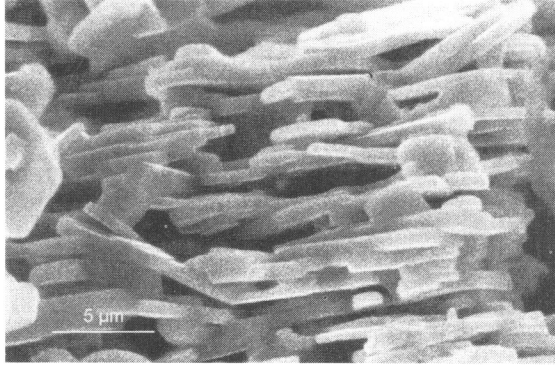


Fig. 6: Small textured domains observed in agglomerates of a pulverized pellet heated at 940°C for 1 h.

the formation of secondary phases, especially (Ca,Sr)-cuprates due to an incomplete re-precipitation process.

For the interpretation of the growth kinetics, the isothermal grain-growth-model [11] was used,

$$\sigma = At^n, \quad (1)$$

where  $\sigma$  denotes the average grain size,  $A$  a constant that exhibits an Arrhenius temperature dependence,  $t$  the time and  $n$  the grain growth exponent. With respect to the initial grain size,  $\sigma_0$ , the following relations were applied

$$\sigma^m - \sigma_0^m = at^* \quad \text{and} \quad (2)$$

$$\sigma = (at^* + \sigma_0^m)^{1/m}, \quad (3)$$

where  $m=n^{-1}$  and  $\sigma_0$  denotes the grain size at  $t^*=0$ . Considering equations (1) and (3) the grain-growth-model equation can be written as

$$\sigma = A(t^* + t_0)^n, \quad (4)$$

where  $t_0$  corresponds to the time needed to grow grains of a size of  $\sigma_0$ , and  $t = (t^* + t_0)$ . With  $\sigma_0^m = A^m t_0$  and  $a = A^m$ , the parameter  $t_0$  can be calculated from the initial grain size from the relation  $t_0 = (\sigma_0^m)/a$  by a fit of equation (2). Based on the logarithm of equation (4), the slope (see Fig. 7) yields the exponent  $n$  and the intersection with the ordinate axis the rate constant  $A$ .

In most ceramic systems, the grain growth exponent,  $n$ , is smaller than 0.5 [11,12] due to the existence of pores, inclusions of secondary phases, grain segregation, and non-stoichiometry which

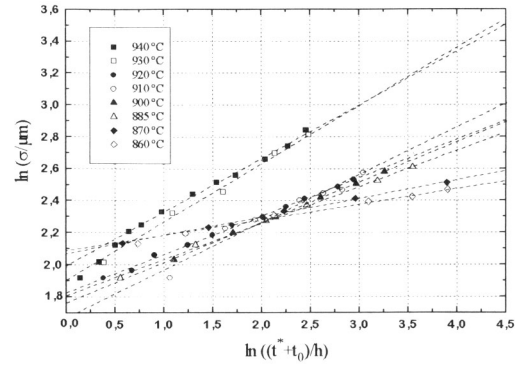


Fig. 7: Double-logarithmic plot of the measured average grain size versus corrected sintering time.

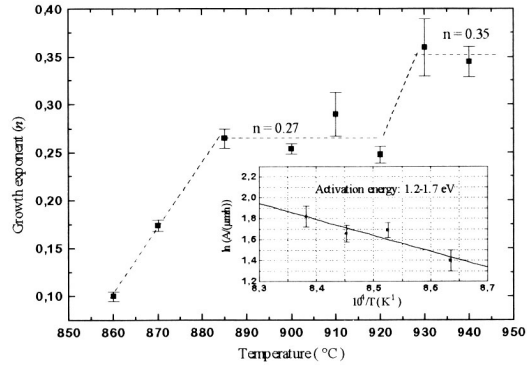


Fig. 8: Temperature dependence of the grain growth exponent. The inset presents an Arrhenius temperature dependence of the rate constant  $A$ , corresponding to an activation energy for the grain boundary motion of 1.2-1.7 eV.

increases the energy necessary to move grain boundaries and inhibits grain growth. Another factor that may highly influence growth exponent is the presence of a liquid phase. It has been observed for other HTSC-ceramics [13,14], that the grain growth follows a cubic law ( $n = 1/m = 1/3$ ) which corresponds to the coexistence of a liquid. Fig. 8 shows the dependence of the exponent  $n$  on the annealing temperature. With increasing temperature the exponent  $n$  increases rapidly to a value of about 0.27 at 885°C, remains nearly constant over a wider temperature range and increases again to 0.35 at 930°C.

Below 885°C the grain growth and hence  $n$  is negligible. Above 885°C,  $n$  differs significantly from the ideal value of 0.5 which would correspond to a non liquid process for pure materials (without pores, inclusions, secondary phases etc.). For  $T \geq 930^\circ\text{C}$  the value of  $n$  supported the occurrence of a liquid phase which results in a cubic dependence. The fact that the value of  $n$  between 885°C and 920°C is lower than 1/3 in spite of the observed liquid phase above 885°C might

be attributed to the presence of a very small amount of liquid and partial wetting of the grain surfaces. Furthermore, the formation of plate-like grains during sintering due to highly anisotropic grain boundary energies as discussed by Grest *et al.* [15] would favour such a low  $n$ -value. Therefore, the second increase of  $n$  at about 925°C is apparently related to the onset of another peritectic/eutectic liquid which might correspond to the very small endothermic peak observed at 923°C by DTA.

Since the melting point depends on the composition, up to eight solid and liquid phases, according to the phase rule and considering only cations, may coexist in equilibrium in a sample investigated at constant T and p. Because of this fact and the unknown oxygen partial pressure (diffusion) within the sample, the exact determination of the origin of the incomplete phase formation is very difficult.

From the Arrhenius temperature dependence of the rate constant  $A$  ( $A = A_0 \exp(-Q/KT)$ ), the activation energy,  $Q$ , for grain boundary motion between 885 °C and 920 °C, corresponding to  $n \approx 0.27$ , was determined to be in the range of 1.2-1.7 eV which is considerably lower than values reported for Y-123 (8-11 eV [14]) and Bi-2223 (5-8 eV [16]). Since grain growth simulations [15] suggest that the grain growth exponent is related to the grain boundary energy it can be concluded that the growth rate and hence the grain boundary motion of Tl-1223 are much higher than for Y-123 and Bi-2223.

## Conclusion

The phase formation of  $(\text{Tl}_{0.6+y}\text{Pb}_{0.2}\text{Bi}_{0.2})(\text{Sr}_{1.8}\text{Ba}_{0.2})\text{Ca}_{2-y}\text{Cu}_3\text{O}_{9.8}$  ( $y = 0, 0.1$ ) was analyzed by DTA which revealed at least three endothermic peaks. At 945°C, partial decomposition of Tl-1223 takes place which leads to the formation of Tl-1212 above 963°C. Above 981°C, Tl-1212 is completely melted and represents the main phase. This decomposition makes melt-texturing very difficult. SEM investigations support the presence of a liquid ( $T_p/T_e \approx 885^\circ\text{C}$ ). As expected from grain growth kinetics, this liquid phase enhances the grain growth and texture and leads to the formation of small textured domains. 20µm large plate-like grains could be obtained. The occurrence of a liquid, however, is accompanied by a decrease of the phase purity of the sample, due to an incomplete re-precipitation process

into the Tl-1223 phase, leading to secondary phases, in particular (Ca,Sr)-cuprates.

The grain growth exponent,  $n$ , seems to remain almost constant over a wide temperature window (885 - 920°C).  $n$  differs, however, from the classical value of 1/3 in spite of the coexistence of a liquid phase during sintering due to partial wetting of the grains. The shift of the growth exponent  $n$  to  $\sim 1/3$  at  $\sim 925^\circ\text{C}$  and the small peak observed at a similar temperature by DTA (923°C) apparently correspond to a possible second liquid phase formation. An activation energy for grain boundary motion was evaluated which indicates a much faster grain growth kinetics than for Y-123 or Bi-2223.

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