An efficient and reproducible approach for attaining superconductivity at 128 K in Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10-\delta}$

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We report an efficient, and highly reproducible, method for the preparation of almost single phase Tl-2223 material, which is characterized by high-temperature superconductivity with $T_{\text{c onset}} = 128$ K and $T_{\text{c zero}} = 126$ K as measured by electrical resistivity, and a diamagnetic onset temperature $T_{\text{mag}}$ of 128 K as measured by AC susceptibility. This procedure involves synthesizing a material with nominal stoichiometry Tl$_{1.6}$Ba$_2$Ca$_2$Cu$_3$O$_{10-\delta}$, which was sintered at 910°C for 3 h, annealed at 750°C (10 days) in an evacuated quartz tube, and finally annealed at 600°C (2 h) in a 0.2% oxygen/nitrogen gas mixture. Based on these results, it appears that the optimization of the hole concentration in Tl-2223, achieved here by controlling the oxidizing/reducing power of the annealing atmosphere, appears to be crucially important in attaining such a high transition temperature.

1. Introduction

High-temperature superconductivity in the Tl–Ba–Ca–Cu–O compound was discovered by Sheng and Hermann in 1988 [1]. Soon after, Parkin et al. [2] reported a method for the synthesis of a material Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10-\delta}$ (hereafter referred to as 2223) which exhibited zero resistance and diamagnetism below a temperature of 125 K. The material was prepared by mixing powders of TlO$_3$, BaO, CaO and CuO with a nominal composition of TlBaCa$_3$Cu$_3$O$_y$. After grinding, the mixture was pressed into a pellet, wrapped in gold, and sintered at 880°C for 3 h in a sealed quartz tube containing ~1 atm of oxygen. Due to the off-stoichiometry starting composition (e.g. TlBaCa$_3$Cu$_3$O$_y$), the synthesized material was composed of a major 2223 phase in addition to other impurities, for example Tl$_{0.04}$Ca$_{0.41}$Cu$_{0.55}$O$_y$ [2]. However, it appears problematic to routinely synthesize this 125 K superconducting material. From our experience, we felt that a possible difficulty in this synthetic process was the precise control of oxygen pressure. Recently, Adachi et al. [3] have demonstrated a superconducting transition with zero resistance and diamagnetism below 125 K and 127 K, respectively, in the 2223 phase. The sample was prepared by mixing the powders of Tl$_2$O$_3$, BaCuO$_2$, Ca$_2$CuO$_3$ and CuO with the nominal composition the same as that used by Parkin et al. [2]. After grinding, the mixture was pressed into a rectangular bar, wrapped in gold foil, and sealed in evacuated quartz tube and fired at 760°C for 10 days. Even though the as-synthesized sample has a high superconducting transition temperature, it is still multiphasic, possibly arising from the use of an off-stoichiometry starting mixture. However, we think that this low temperature vacuum annealing provides a very effective means for obtaining a high transition temperature in the 2223 phase; our proposal is that if one can first synthesize single phase 2223 material and then apply this annealing process, this will lead to an improvement in the superconducting properties of the 2223 material.

Kikuchi et al. [4] and Liu et al. [5,6] have reported that by using a stoichiometric composition Tl$_{2-x}$Ba$_2$Ca$_2$Cu$_3$O$_{10-\delta}$ (0.2 $\leq x \leq$ 0.4) where substitution of the Ca ions into the Tl sites occurs, one has an effective method for synthesizing a monophasic 2223 phase. Very recently, Kaneko et al. [7] have also used this stoichiometric composition, Tl$_{1.7}$Ba$_2$Ca$_2$Cu$_3$O$_y$, to prepare single-phase 2223 by...
sintering the mixture at 890°C for 5 h in flowing oxygen. Subsequently, the as-sintered sample was wrapped in gold foil, encapsulated in an evacuated (~10⁻⁴ Torr) quartz tube and annealed at 750°C for 10 days. The resulting sample is nearly single phase and has a superconducting zero-resistance temperature of 126.9 K and a diamagnetic onset temperature of 130 K. These authors [7] suggested that the increase in the superconducting critical temperature may be related to a certain diffusion process, such as ordering of the constituent ions.

In this paper, we demonstrate an efficient procedure to further improve the superconducting transition temperature of single phase 2223 material by low temperature annealing of the sample in a controlled oxygen partial pressure.

2. Experimental

High-purity powders of Tl₂O₃, BaO₂, CaO and CuO were weighed in the appropriate proportions to form nominal compositions of Tl₁₂₋ₓBa₂Ca₂₊ₓCu₃O₁₀₋δ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1.0). The powders were then mixed using a mortar and pestle and pressed into a pellet (10 mm diam. and 3 mm in thickness) under a pressure of 5 ton/cm². The pellets were wrapped in gold foil to prevent loss of thallium at elevated temperatures, then sintered at 910°C for 3 h in oxygen. After sintering, the furnace was cooled to room temperature at a rate of 5°C/min. The sample with x = 0.4 had the highest zero-resistance temperature (120.5 K) among the series. Consequently, we chose the x = 0.4 (i.e. Tl₁₁.₆Ba₂Ca₂₄Cu₃O₁₀₋δ) sample for further investigations. The sample was wrapped in gold foil, encapsulated in an evacuated (~10⁻⁴ Torr) quartz tube and annealed at 750°C for 10 days. The resulting sample was then annealed in 0.2% and 2% oxygen/nitrogen atmosphere at 600°C for 2 h and rapidly quenched into liquid nitrogen. Bar-shaped samples (1.5×2×10 mm) were cut from the annealed pellets and used for resistivity measurements.

X-ray diffraction (XRD) analyses were performed using a Philips PW1710 X-ray diffractometer with a Cu Kα radiation. A standard four point probe method was used for the electrical resistivity measurements. The electrical contacts to the sample were made by fine copper wires with a conductive silver paint; the applied current was 1 mA. The temperature was recorded using a calibrated (accuracy ±0.01 degree) silicon diode sensor located close to the sample. The AC magnetic susceptibility was measured using a Lake Shore 7000 susceptometer with a frequency of 333.3 Hz and applied magnetic field of 1 Oe.

3. Results and discussion

In fig. 1 we show the powder X-ray diffraction (XRD) pattern of the as-sintered Tl₁₁.₆Ba₂Ca₂₄Cu₃O₁₀₋δ sample. Most of all the XRD peaks in the sample could be indexed to a 2223 phase having a tetragonal unit cell (P4/mmm) with dimensions 3.857×3.857×35.67 Å. Following the vacuum and oxygen partial pressure heat-treatments, the samples showed no dominant impurity phase in the XRD patterns.

In fig. 2 we show the temperature dependence of the resistivity of the as-sintered (A) Tl₁₁.₆Ba₂Ca₂₄Cu₃O₁₀₋δ sample, that from the vacuum-annealed sample (B), that from the sample annealed in the 0.2% oxygen/nitrogen atmosphere (C), and finally that from the sample annealed in the 2% oxygen/nitrogen atmosphere (D). The zero-resistance temperature, $T_{c,\text{zero}}$ of the as-sintered sample was 120.5 K which was higher than that reported by Kaneko et al. [7] for an as-sintered sample having a nominal composition of Tl₁₁.₇Ba₂Ca₂₃Cu₃O₁₀₋δ with $T_{c,\text{zero}} = 117.9$ K. Our sample after vacuum-annealing had a zero resistance temperature of 124.5 K as compared to a value of 120.5 K for the as-sintered one, see inset of fig. 2, curves A and B respectively. This improvement of the superconducting transition temperature agreed with previous reports [3,7] but we found slightly lower values than those reported by Adachi et al. [3], 124.9 K, and Kaneko et al. [7], 126.9 K. Believing this sample to be underdoped relative to maximum $T_c$, we then attempted to oxidize the vacuum-annealed sample in a partial oxygen pressure of 0.2% and 2% in nitrogen. When the vacuum-annealed sample was oxygenated in the 0.2% oxygen/nitrogen atmosphere, the $T_{c,\text{zero}}$ increased from 124.5 K to 126.0 K, see curve C in inset of fig. 2. This appears to be an optimally doped sample.
When the same sample was further oxygenated in a 2% oxygen/nitrogen atmosphere, the $T_c \text{zero}$ was reduced to 125.7 K, compare curves C and D in inset of fig. 2.

In fig. 3 we show the temperature dependence of the normalized AC susceptibility (taking the limiting, low temperature (5 K) values as $-1$) of the powdered $\text{Tl}_{1.6}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-\delta}$ sample after annealing in the 0.2% oxygen/nitrogen atmosphere. The onset of diamagnetism, $T_{c\text{mag}}$, appeared at 128 K (see inset, fig. 3) and this was consistent with the $T_{c\text{mid-point}}=128$ K, measured from the resistivity curve C (fig. 2). Under these synthetic conditions, the superconducting transition beginning at 128 K is very stable over a period of months, and reproducible.

Based on our previous studies [8,9], the oxygen stoichiometry ($\delta$) has a major effect on the superconducting transition temperature in $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-\delta}$. For example, a decrease in $\delta$ arising from annealing the sample at lower temperatures in oxygen results in an increase in $T_c$. These observations led us to conclude that an increase in the hole concentration in as-sintered samples may
lead to possible improvements in $T_c$ for the 2223 phase.

For the present systems, the weight loss between the as-sintered and low temperature vacuum-annealed samples is about 5%. According to our previous studies [8,9], we found that the oxygen loss at 750°C for Tl-2223 phase is less than 0.1%. Consequently, we propose that Tl loss may be the major contributing factor to the weight loss of 5%. The small amount of oxygen loss would lead to a decrease in the hole concentration in the 2223 phase. In contrast, any thallium loss (e.g. during low temperature vacuum annealing) would create cation vacancies and subsequently increase the hole concentration in the 2223 phase. Some support for this proposal comes from the observation of a decrease in the normal state thermopower values when one compares the values before and after vacuum annealing [10]. The proposed increase in the hole concentration in the 2223 phase after the low temperature vacuum annealing may be responsible for an increase in $T_c$. If this is the case, one still has the opportunity to further increase the hole concentration by annealing the compound in a partial oxygen pressure; this would naturally compensate for any oxygen loss occurring from the vacuum annealing process. Based on this hypothesis, we have found that the optimizing oxygen partial pressure of 0.2% in nitrogen is effective in increasing the $T_{c_{\text{zero}}}$ from 124.5 K to 126 K. More detailed investigations of the normal state thermopower and Hall measurements are currently underway.

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**References**