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# Critical Currents of $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_z$ Bulk Superconductors

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The critical temperatures and the critical currents of  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_z$  (Tl-2223) bulk superconductor have been studied using ac susceptibility measurements before and after the oxygenation process. With oxygenation the critical temperature increased from 114.2 K to 118.8 K and the critical current at 77 K raised from 56 A/cm<sup>2</sup> to 230 A/cm<sup>2</sup>. The Ginzburg–Landau strong coupling limit approach was applied to describe the temperature dependence of the critical current densities.

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## 1. Introduction

Thallium based superconductors exhibit one of the highest critical temperatures among the high temperature superconductors. A very important and prospective is that the critical temperatures of some compounds of this family can exceed boiling point of the natural gas ( $T_b = 111.5$  K) which enables these compounds to work as superconductors in LNG environment.

The critical temperature of cuprate superconductor depends on the number of oxygen–copper ( $\text{CuO}_2$ ) layers in the superconductor primitive cell [1]. For thallium based superconductors of the homologous series  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_z$  (Tl-22(n-1)n) the critical temperature achieves its maximum, 125 K, for three layer compound ( $n = 3$ ) [2, 3]. The maximum critical temperature predicted theoretically for double-thallium cuprate is 146 K [4]. The critical temperatures of bulk Tl-2201 [5], Tl-2212 [6] and Tl-2234 [7] are 90, 118, and 116 K, respectively. For  $\text{Tl}_1\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_z$  (Tl-12(n-1)n) homologous series the maximum critical temperature is of the order of 120 K and occurs also for three oxygen–copper layers [8]. The critical temperatures for these system depend also on some other factors. The first of them is the oxygen parameter [9]. It can be modified by annealing the sample in oxidizing or reducing atmosphere [6] or sintering the sample for various times and at various temperatures [9]. The second factor are the element substitutions [10]. They can also stabilize the phase which is going to be obtained [11]. Phase stabilization means optimization of the oxygen stoichiometry and maximization of the critical temperature. Substitutions have their influence on the critical temperature of the superconducting phase [10]. Critical current densities ( $J_c$ ) of thallium based superconductors can vary in a wide region. They range from 400 A/cm<sup>2</sup> of  $\text{Tl}_1\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_z$  ceramic samples [12] to 0.5 MA/cm<sup>2</sup> of

$(\text{Tl}_{0.6}\text{Pb}_{0.24}\text{Bi}_{0.16})(\text{Ba}_{0.1}\text{Sr}_{0.9})_2\text{Ca}_2\text{Cu}_3\text{O}_y$  film on single-crystalline lanthanum aluminate [13]. The thallium 1212 bulk samples partially doped with Gd for Ca have critical current densities up to 4 kA/cm<sup>2</sup> [14]. The highest critical current density at 77 K was achieved for composition  $\text{Tl}_{0.52}\text{Pb}_{0.5}(\text{Sr}_{0.95}\text{Ba}_{0.05})_2(\text{Ca}_{0.8}\text{Gd}_{0.2})\text{Cu}_2\text{O}_z$ . A small change of composition or the sintering temperature can considerably decrease the critical current density.

In this work we have investigated how annealing in oxygen affects the critical temperature and the critical current densities of the ceramic  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_z$  superconductor. Oxygenation for 20 h at 740 °C was carried out to improve the properties of the Tl-2223 sample studied.

## 2. Experimental

The appropriate amounts of  $\text{BaCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{CuO}$  were used to synthesize the precursors. At the beginning  $\text{BaCuO}_2$  and  $\text{Ca}_2\text{CuO}_3$  precursors were synthesized at the same thermal conditions. After careful grinding, the precursors were calcined at 840 °C for 24 h and next, at 940 °C for 48 h in one heating procedure. Then, the precursors were ground and in the second step precursors were calcined at 940 °C for 48 h to obtain monophasic oxides. Then, the precursors were thoroughly reground again. Appropriate amounts of the precursors and  $\text{Tl}_2\text{O}_3$  have been mixed for ten minutes in the third step of the synthesis. Then, a pellet was formed under the pressure 4.4 kbar and wrapped in a silver foil that prevents thallium from leaving the wrapped sample. On the other hand, silver foil is permeable for oxygen in elevated temperatures [15, 16]. What is more silver is a noble metal and does not react in the furnace as fast as for example copper. (Copper foil heated in oxygen in 900 °C becomes fragile and loses lustre.)

The detailed procedure of the third step was as follows. The pellet was put in the hot furnace of the temperature 900 °C and 0.6 bar oxygen flow. This furnace temperature was held for four minutes. Then the temperature inside the furnace was increased with ramping ratio of 5 °C/min for three minutes, to reach 915 °C. This temperature was held for the next 38 min. Altogether, in the

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third step, the wrapped pellet was annealed for 45 min in oxygen atmosphere. After that the pellet was removed from the hot furnace. A part of the sample was next annealed for 20 h at 740 °C in oxygen.

AC susceptibility measurements were carried out using mutual inductance bridge method in ac magnetic fields up to 10.9 Oe. The dispersion (real) part and the absorption (imaginary) parts of ac susceptibility were measured separately. The device was operating at the frequency 189 Hz. A Stanford SR 830 lock-in nanovoltmeter served both as a source of the ac current for the coil producing the ac magnetic field and as a voltmeter of the bridge. The temperature was monitored by a Lake Shore temperature controller employing a chromel–gold–0.07%iron thermocouple with the accuracy of  $\pm 0.05$  K. The sample studied has a flat parallelepiped shape and the ac magnetic field was parallel to its largest surface.

### 3. Results and their analysis

Analysis of the XRD patterns showed that the sample contains two superconducting phases: the majority 2223 superconducting phase and a minority 2201 superconducting phase. The sample was found to contain unreacted and non-conducting phases: CaO and  $BaCuO_2$ . The dispersion and absorption parts of ac susceptibility of the ceramic  $Tl_2Ba_2Ca_2Cu_3O_z$  before and after the oxygenation obtained at various ac magnetic fields are shown in Fig. 1a,b and Fig. 2a,b, respectively. The critical temperatures (for illustration of the way of the critical temperature determination — see inset in Fig. 3) of the sample were obtained from the dispersion parts of ac susceptibility and they are  $T_c = 114.2$  K before and  $T_c = 118.8$  K after the oxygenation. It means that the critical temperature was increased by 4.6 K during 20 h oxygenation. In similar conditions [17] (750 °C, sample in sealed quartz tube) the susceptibility critical temperature raise was 4.0 K for 10 h annealing and 5.0 K for 80 h annealing.

In Fig. 1b and Fig. 2b for higher amplitude of ac magnetic fields intergrain absorption peak moves its position to lower temperatures and the intragrain peak becomes visible. Intragrain peak position is practically field independent and this peak appears at higher temperatures than the intergrain peak. For lower fields these two peaks are not separated and largely overlap.

In Fig. 2a one can observe that the transitions to superconducting state are narrower than in Fig. 1a. As a consequence, the absorption peaks in Fig. 2b are also narrower and their positions are shifted to higher temperatures with respect to the peaks in Fig. 1b. A comparison of the dispersion and absorption parts of the ac susceptibility as a function of temperature for the sample before and after oxygenation are shown in Figs. 3 and 4. The measurements were carried out at the 0.218 Oe of the ac field amplitude. The shape of the dispersion curve is more steep for the oxygenated sample (Fig. 3). In the case of the absorption part of ac susceptibility the

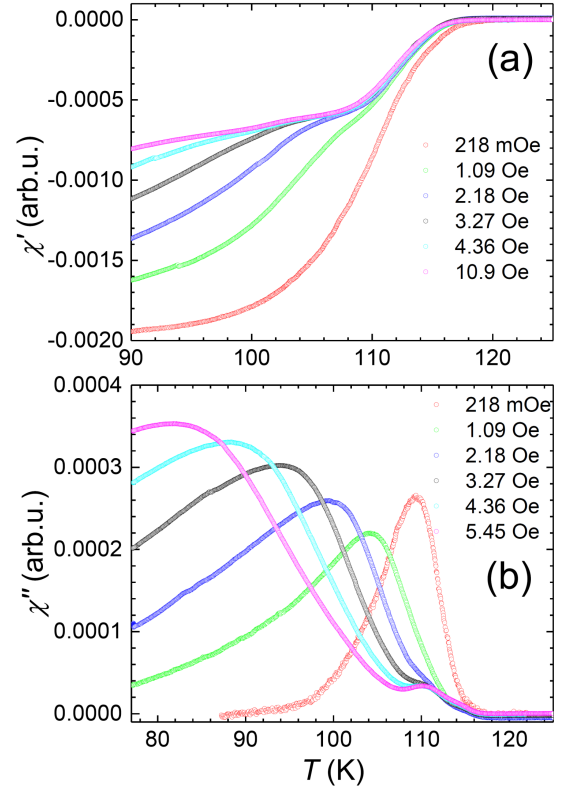


Fig. 1. Temperature dependence of the ac susceptibility of the  $Tl_2Ba_2Ca_2Cu_3O_z$  superconductor before oxygenation at selected magnetic field values: (a) the real part and (b) the imaginary part.

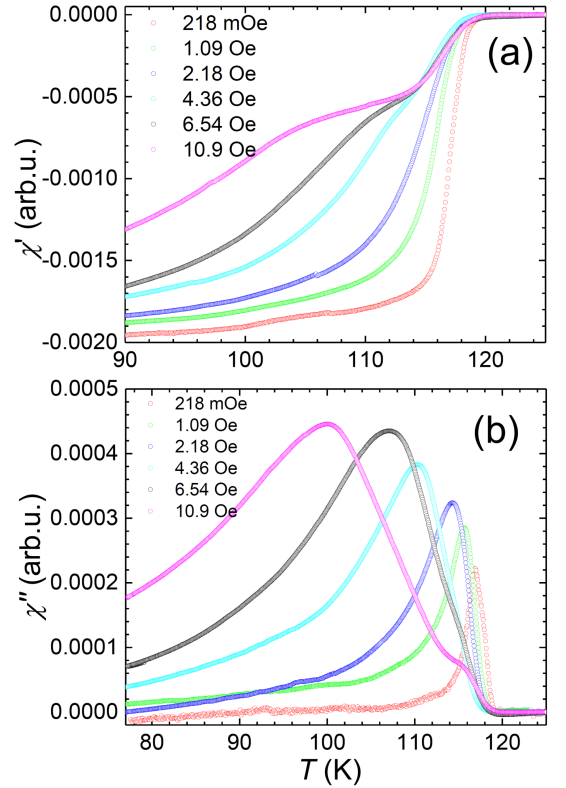


Fig. 2. As in Fig. 1, but after oxygenation.

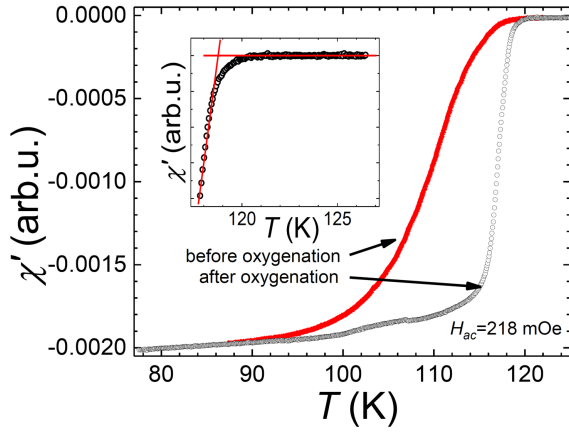


Fig. 3. A comparison of the critical temperatures derived from the susceptibility measurements for the sample before and after oxygenation. Measurements were done at  $H_{ac} = 0.218$  Oe. Inset: illustration of the way of the critical temperature determination.

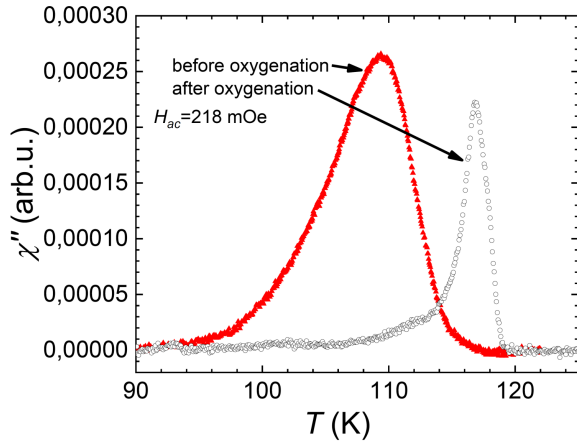


Fig. 4. A comparison of the susceptibility absorption parts for the  $Tl_2Ba_2Ca_2Cu_3O_z$  superconductor before and after oxygenation. Measurements were carried out in  $H_{ac} = 0.218$  Oe.

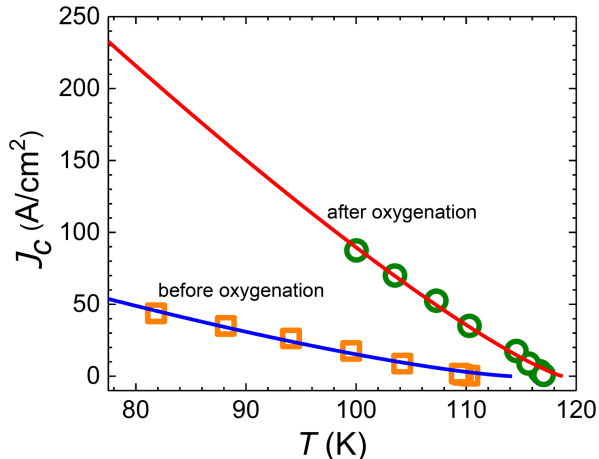


Fig. 5. Critical current densities derived with Bean's model for the  $Tl_2Ba_2Ca_2Cu_3O_z$  superconductor before (open squares) and after (open circles) oxygenation. The solid lines are the fit to (2).

intergranular peak was much narrower after oxygenation (Fig. 4). The temperature dependence of the critical current density was obtained from the ac susceptibility measurements within the Bean critical state model. Taking advantage of the temperature dependence of the absorption peaks the critical current density can be expressed by the following formula [18, 19]:

$$J_c = \frac{2H_{ac}}{d}, \quad (1)$$

where  $H_{ac}$  is the ac magnetic field amplitude and  $d$  is the thickness of the sample.

The obtained critical current densities are shown in Fig. 5. Their temperature dependences were fitted using the Ginzburg–Landau strong coupling limit approach given by formula [20]:

$$J_c = J_{c0} \left(1 - \frac{T}{T_c}\right)^n, \quad (2)$$

where  $J_{c0}$  and  $n$  are parameters fitted and  $T_c$  is the critical temperature obtained from the experiment. The exponent  $n$  was determined to be of 1.5 [21, 22]. Its value greater than unity means that we deal with a vortex glass structure and strong pinning. A positive curvature of the function from Eq. (2) is typical for high temperature superconductors. The critical current may be limited when the pinning force is weak, which would be indicated by the exponent  $n$  smaller than unity. Making use of the fitted parameters the critical current density values were calculated at the liquid nitrogen temperature and they are  $J_c = 56$  A/cm<sup>2</sup> and  $J_c = 230$  A/cm<sup>2</sup> before and after oxygenation, respectively (see solid lines in Fig. 5). This means that the critical current increases more than four times after the oxygenation process. Values of the order of several hundreds A/cm<sup>2</sup> are typical values for ceramic thallium based superconductors [12]. A significant increase of critical currents up to the order of MA/cm<sup>2</sup> takes place for thin-film systems of these superconductors [23–25]. Superconducting thallium based filaments can have critical current density up to 2.3 kA/cm<sup>2</sup> [26] or 12 kA/cm<sup>2</sup> [27]. Although the starting filament composition was Tl-2223, the resulting composition was Tl-1223 due to the thallium oxide volatility. The parameter  $n$  changes from 1.33 before oxygenation to 1.21 after oxygenation. Its values are greater than unity, so we have the case of a strong pinning in the  $Tl_2Ba_2Ca_2Cu_3O_z$  superconductor studied and the pinning force decreases with heating of the material in oxygen.

#### 4. Conclusions

Oxygenation at 740 °C for 20 h in flowing oxygen results in a higher critical temperature and a higher critical current density of the  $Tl_2Ba_2Ca_2Cu_3O_z$  bulk superconductor. The critical temperature increased from 114.2 K to 118.8 K and the critical current density raised from 56 A/cm<sup>2</sup> to 230 A/cm<sup>2</sup> as a result of oxygenation. The  $n$  parameter was found to correspond to vortex glass structure at strong pinning and it decreased from 1.33 before, to 1.21 after oxygenation.

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