EFFECTS OF POST-OXYGEN ANNEALING AND LANTHANUM DOPING ON INTER- AND INTRA-GRAIN PROPERTIES OF (Tl,Pb)-1223 SUPERCONDUCTORS

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Submitted September 17, 2004; accepted November 3, 2004

Keywords: (Tl,Pb)-1223 based superconductors, La^{3+} doping, Magnetization, SQUID gradiometer, Ageing

Effects of oxygen annealing and low level La^{3+} doping of the (Tl,Pb)-1223 system have been investigated. Samples with the nominal composition $(Tl_{0.6}Pb_{0.5})(Sr_{0.8}Ba_{0.2})_2Ca_2Cu_3O_{8+\delta}$ - x $LaO_{1.5}$, where x ranges from 0.00 to 0.10, were synthesized using a sol-gel process. Their superconducting inter- and intra-grain properties, phase compositions, and microstructure were studied. XRD results prove that (Tl,Pb)-1223 is the dominant phase in all samples. The La doping initiates a formation of the (Tl,Pb)-1212 phase and decreases the volume superconducting properties. The post oxygen annealing strongly improves inter-grain superconducting links and leads to a positive effect on the critical temperature, T_c^{on} and the ΔT_c^{on}. The central peak of magnetization hysteresis loops around zero field is found to be in an anomalous positive position on the descending branch of the external field.

INTRODUCTION

Thallium-based cooper oxide superconductors with critical transition temperatures above 100 K represent a real opportunity for applications at about 77 K. It is well-known that weak links located at the grain boundaries and magnetic flux pinning are two important limiting problems which determine relevant application properties such as the critical current density j_c(H), the critical and irreversible magnetic fields, the levitation force, etc. Magnetic measurements are valuable tool for studying all such properties. Among the Tl-based superconductors, the Tl-1223 phase with Tc value of ~115 K is the most promising one. In our previous paper [1], the effects of the heterovalent substitution of rare earth ions RE = La^{3+}, Sm^{3+}, Pr^{3+}, Dy^{3+} and Y^{3+} into the Ca^{2+} separating layers on the magnetic properties of $(Tl_{0.6}Pb_{0.5})(Sr_{0.8}Ba_{0.2})_2(Ca_{1-x}RE_x)_2Cu_3O_{8+\delta}$, superconductor were investigated. The increasing content of the rare earth elements increased the amount of (Tl,Pb)-1212 admixed phase in the substituted samples and led to a decrease in the critical temperature. We observed that La^{3+} deteriorated the grain properties to the least extent of all RE substituting elements. On the other hand, improvements of some inter-grain properties for small La^{3+} doping level could be observed.

In order to understand the role of lanthanum addition in the Tl/Pb-Sr/Ba-Ca-Cu, (Tl,Pb)-1223 phase, which is a promising candidate for near-term practical applications, we performed study of the $(Tl_{0.6}Pb_{0.5})(Sr_{0.8}Ba_{0.2})_2Ca_2Cu_3O_{8+\delta}$ - x $LaO_{1.5}$ system. In this paper, we describe effects of oxygen annealing and lanthanum addition in the above system, where x ranges from 0.00 to 0.10, on inter and intra-grain properties. Series of the samples were prepared for every concentration level x of the lanthanum oxide. The results presented are characteristic for all sets of the samples.

EXPERIMENTAL

The bulk samples were prepared in two-step process using the Sr-Ba-Ca-Cu-O precursor synthesized by a sol-gel technique. Before pressing into pellets, proper amounts of PbO, Tl_2O_3 and La_2O_3 were added to the precursor. The samples were sintered in flowing oxygen at 925°C for 12 min followed by a heat treatment at 910°C for 10 h. The final post-annealing of some of the as-sintered samples was carried out in flowing oxygen at 750°C for 50 h. The critical temperature of the samples was determined by a standard resistance four-point method T_c (R = 0) and also by a mutual inductance technique using Meissner shielding

Paper presented at the conference Solid State Chemistry 2004, Prague, September 13 -17, 2004.

current [3]. In the last case, the critical temperature T_c^{on}, was determined as the temperature, at which the onset of diamagnetic behavior was observed. The transition width was characterized by 10-90% criteria. The phase composition was studied by X-ray diffraction measurements (CuKα radiation) from powdered samples. The microstructure of the samples was investigated by a scanning electron microscopy, EDX microanalysis and optical polarization microscopy.

AC and DC virgin volume magnetization characteristics were measured in detail by a compensation method using the second-order SQUID gradiometer [3]. All magnetization characteristics of the samples were measured at 77.3 K after the zero-field cooling in magnetic fields ranging from 10^{-1} to 10^5 A/m. For AC magnetization measurements, the frequency of 0.1 Hz was used. An applied magnetic field, H_a, was gradually increased for five amplitudes for each chosen range of field. The applied magnetic field was parallel to the axis of the sample. The demagnetizing factor was determined from the geometry of the sample. The first penetration magnetic field H_{pl}^{wl} of the intergrain weak link network and the magnetic susceptibility χ were determined from the linear behavior of the virgin DC magnetization curves in the region of the full Meissner shielding of the entire sample. H_{pl}^{wl} was evaluated from the first deviation from linearity of the virgin DC magnetization curves measured in the appropriate range of the magnetization field, e.g., typical for displaying the intergrain properties.

RESULTS AND DISCUSSION

Generally, the obtained results show that the typical T_c values of parent as-sintered samples (without La) were about 113 K and ΔT_c ~2.8 K. The doping with lanthanum oxide resulted in an increase in characteristic values of T_c by about 2 K for all doping levels and at the same time in a decrease in ΔT_c by about ~0.5 -0.8 K. However, a weak regress in this tendency is evident for the highest La content, x = 0.1. Figure 1 shows the temperature dependence of the induced voltage normalized to the voltage value at 200 K of the $(Tl_{0.6}Pb_{0.5})(Sr_{0.8}Ba_{0.2})_2Ca_2Cu_3O_{8+\delta}$ - x $LaO_{1.5}$ samples before and after the post-annealing in flowing oxygen for various nominal La-contents. The highest value of T_c ~116.8 K and the smallest ΔT_c ~1.9 K were observed for doping level x = 0.04 in as-sintered samples. The post-oxygen annealing led to a positive effect on the critical temperature T_c^{on}, and the transition width ΔT_c^{on}, but at the same time, significant differences between the values of T_c and T_c^{on}, as well in transition widths appeared. The temperature dependence of electrical resistance of several samples shows a broad tailing (R ~ 0) following after the original sharp transition of the resistance at lower temperatures. After the post-annealing in oxygen atmosphere, the T_c^{on} values of the samples increased by about 3-4 K, and ΔT_c^{on} decreased mainly for values of x = 0 and 0.04. The La-doping level x = 0.04 led to the best values of T_c^{on} ~119.5 K and ΔT_c^{on} ~0.8 K.

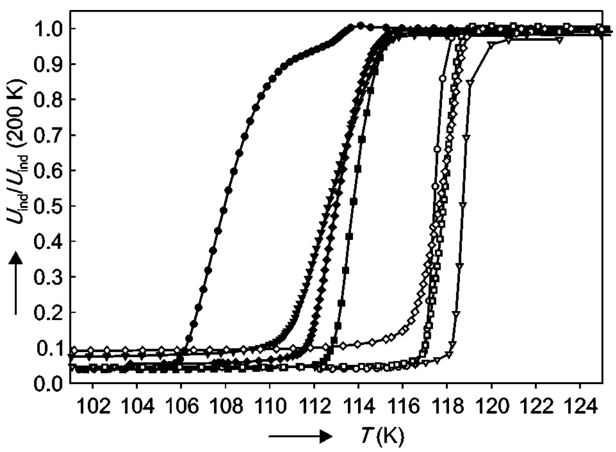


Figure 1. The temperature dependence of the induced voltage normalized to the voltage value at 200 K of the $(Tl_{0.6}Pb_{0.5})(Sr_{0.8}Ba_{0.2})_2Ca_2Cu_3O_{8+\delta}$ - x $LaO_{1.5}$ samples before (filled symbols) and after (open symbols) the post-annealing in flowing oxygen at 750°C for 50 h. The nominal La-contents x = 0, 0.04, 0.07 and 0.1 are designated by circles, triangles, squares and diamonds, respectively.

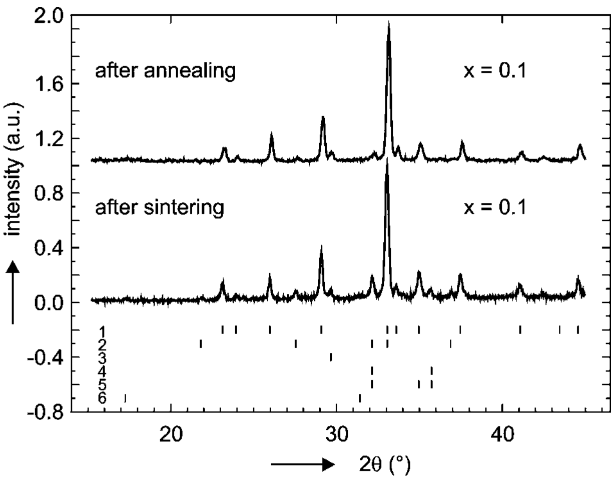


Figure 2. X-ray powder diffraction patterns for the samples with the nominal $LaO_{1.5}$ level, x = 0.1, after the post-annealing in flowing oxygen. Bars indicate peak positions of the (Tl,Pb)-1223 phase (1), the (Tl,Pb)-1212 (2), $BaPbO_3$ (3), Ca-Sr-cuprate phases (4,5) and Sr-Ca-plumbate phase (6).

Based on the analysis of powder diffraction data, it can by concluded that the dominant phase is (Tl,Pb)-1223, the minority phases are (Tl,Pb)-1212, and the insulator phase $BaPbO_3$ is present in all samples (either sintered, or annealed) (figure 2). Small amounts of the secondary phases (together - less than 4 %) of Ca-Sr-cuprate and Sr-Ca-plumbate could be found in as-sintered samples. An increase in the La content leads to rise of the volume of the (Tl,Pb)-1212 phase in both sintered and post-annealed samples. Data from the ICSD were used in the analysis of diffraction data, and the Powder Cell 2.4 program (written by W. Kraus and G. Nolze) was used in calculations [4]. Detailed results will be published in a following paper. A typical AC magnetization hysteresis loops of as-sintered and post-annealed samples with no lanthanum oxide (x = 0) for five amplitudes of magnetizing field are shown in figures 3 and 4.

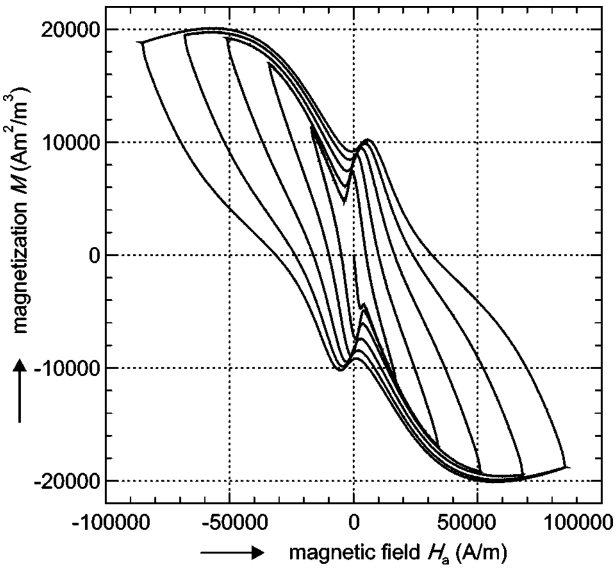


Figure 3. AC magnetization M vs. the applied field H_a of an as-sintered sample of the nominal composition of $(Tl_{0.6}Pb_{0.5})(Sr_{0.8}Ba_{0.2})_2Ca_2Cu_3O_{8+\delta}$ for five amplitudes of H_a.

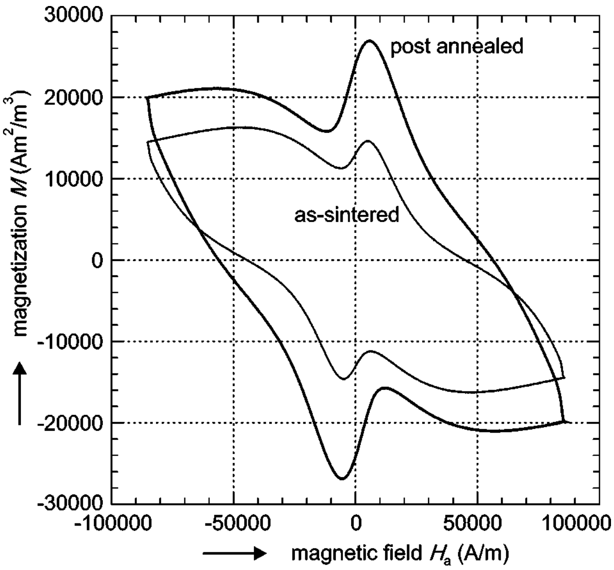


Figure 5. Comparison of the envelope magnetization hysteresis cycles of the typical as-sintered and post-annealed samples with a doping content of x = 0.1.

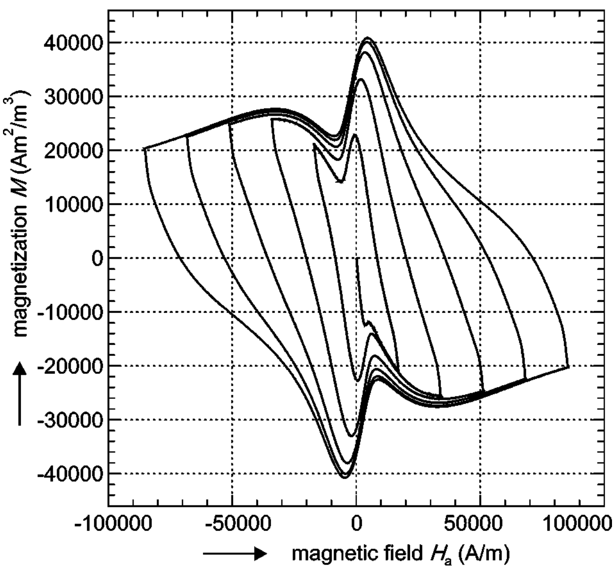


Figure 4. AC magnetization M vs. the applied field H_a of a sample of the nominal composition of $(Tl_{0.6}Pb_{0.5})(Sr_{0.8}Ba_{0.2})_2Ca_2Cu_3O_{8+\delta}$ for five amplitudes of Ha after the post-annealing in flowing oxygen.

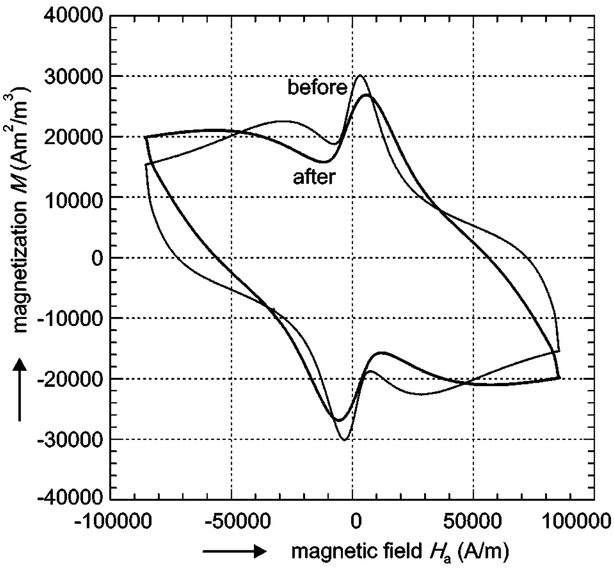


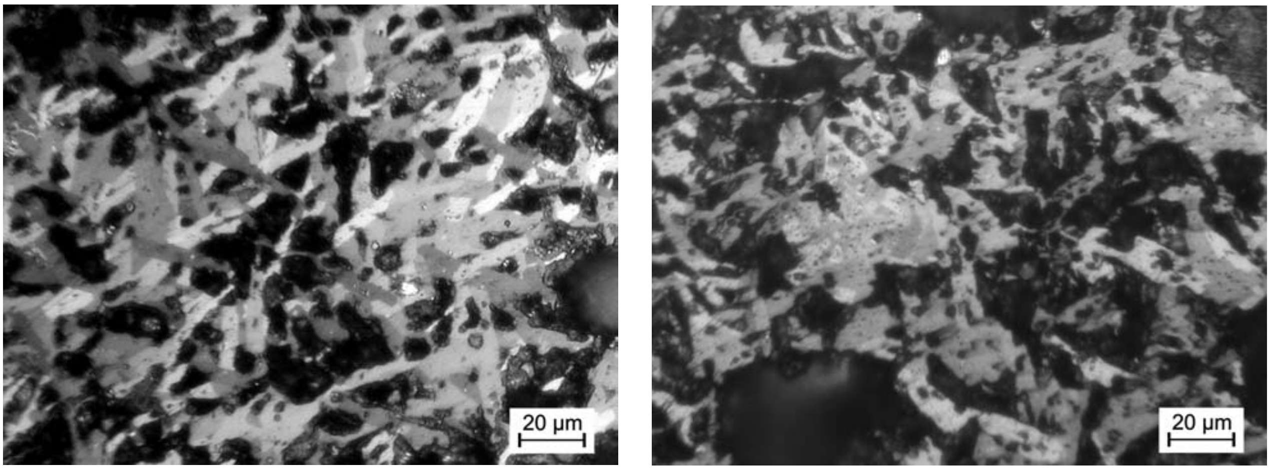
Figure 6. Comparison of the envelope magnetization hysteresis loops of a typical post-annealed sample with added lanthanum oxide x = 0.1 before and after the expiration of 28 months.

Comparing the results of the two figures, sharp changes in the shape and mainly in the hysteresis of magnetization loops can be seen. As the magnetization hysteresis is a direct gauge of the critical current density, it can be concluded that the post-annealing in oxygen leads to a significant increase in the critical current density of the samples, especially in the range of the zero field ($H_a \sim 0$). The central peak of magnetization loops around the zero field corresponds mainly to intergrain properties. This means that the post-oxygen annealing significantly improves current properties of intergrain superconducting links, and thereby also the shielding of the whole volume of the samples with low field branch. This can also be applied to all samples with added lanthanum oxide (figure 5).

Generally, there is a lack of information related to ageing effects of high temperature superconducting materials, especially with regard to the Tl-based superconductors. After the preparation of samples, some characteristics of our samples were repeatedly measured. The samples were usually stored in a desiccator, however, during the measurements, sometimes lasting for several weeks, they were unprotected against the atmosphere moisture and temperature shocks when immersing into LN_2 and returning back to the room temperature. Figure 6 compares the envelope magnetization hysteresis loops of the same post-annealed sample without lanthanum-doping measured before and after the expiration of 28 months. Differences of the shape and hysteresis of magnetization curves indicate that the long time interval again led to a weak decrease in the critical current density or to a degradation of its j_c(H) dependence. It can be seen mainly in the area of a higher field, where the contribution of grain or strong link grain clusters in magnetization can be expected. Therefore, the shape of the magnetization curve of the sample after 28 months implies noticeable changes in j_c(H) dependence of the sample, which can be related to changes of the grain surface and/or cluster intergrain connection properties.

The shape of magnetization hysteresis loops of our samples is interesting also with regard to another aspect. It is the position of central (or low-field) peaks of the hysteresis loops which are found to be anomalously shifted towards a positive field on the decreasing branch (and towards a negative field on the increasing branch) of the hysteresis loops. Thus the peaks occur before the zero external field H_a is reached. Generally, high-T_c superconductors show a central magnetization peak at negative field values on the descending branch of the hysteresis loop. The anomalously positive position of the central peak has been reported in the Bi-2223 mono- or multifilamentary tapes, or in model thin film samples with artificially introduced granularity [5-7]. We think that "granularity" of current paths and mainly the comparable contribution of inter- and intra-granular currents to total magnetization near the zero applied field are responsible for the positive position of the central peak in studied bulk (Tl,Pb)-1223 samples.

The analysis of the microstructure of our samples shows well connected plate-like grains with inclusions and the average size of about 6.5 μm. The average anisotropy rate is about 3:1, and a significant effect of La^{3+} doping can be observed. The increasing of lanthanum content leads to an impairment of the rectangular shape of grains and to an increase in the amount of intragrain inclusions and cracks. Figure 7 shows the microstructure of the post-annealed samples without and with lanthanum addition (x = 0.1). The results of microstructural investigations are in accordance with the magnetization measurements results. The values of magnetization and magnetization hysteresis decrease



a) b)

Figure 7. Optical microphotographs (in parallel configuration of polarizers) of the post-annealed $(Tl_{0.6}Pb_{0.5})(Sr_{0.8}Ba_{0.2})_2Ca_2Cu_3O_{8+\delta}$ - x $LaO_{1.5}$ samples with doping levels x = 0.0 (a) and 0.1 (b).

with increasing grain and/or grain cluster disintegration caused by rising La level. Nevertheless, strong intergrain connections still have to be present. They explain relative good magnetic field penetration properties - significantly high values of the first penetration magnetic field H_{pl}^{wl}. The values are still about 4700 A/m at 77 K even in the samples with doping level x = 0.1. The values are comparable with those in melt-textured YBCO samples of corresponding sizes, prepared through the PMP (powder melting process) [8].

Based on significant differences of volume magnetization caused by La doping, we believe that lanthanum presence must directly affect the properties of the dominant (Tl,Pb)-1223 phase. With respect to cation sizes, it could be expected that La^{3+} enters in Ca^{2+} position. The substitution of some La^{3+} for Ca^{2+} can affect not only the axial lengths but also the number of holes and, hence, the carrier concentration in Cu-O planes. The XRD analyses show no significant changes of unit cell of the phase with the doping. However, in relation to this, effects of charge reservoir Tl-O layer could also be significant, as presented, e.g., by B. Morosin at el. [9]. They suggested that Tl^{1+} and Tl^{3+} were present in Tl-O layers of Tl-1223 and as Tl^{1+} is oxided to Tl^{3+} e.g., by oxygen annealing, the Tl-O layer must become thinner and the Tl^{1+}/Tl^{3+}conversion in Tl-O can have small effect on the superconductivity in the Cu-O planes. Observed tiny changes in the critical temperature with La -doping could be consistent with this. In addition, as it has been reported by others, also partial substitutions of Tl-Ca, Ca-Sr, Tl-Ba systematically occur in Tl-based superconductors. With regard to magnetization, only a decrease in the content of the dominant (Tl,Pb)-1223 phase itself is insufficient for the explanation of changes in the magnetization hysteresis (the critical current density) La doped samples. There must be an existence of other effect(s) of the La doping, e.g., a loss of integrity and/or decreasing of a current properties or of the size of shielding current paths or a decrease in structural defects of the (Tl,Pb)-1223 phase, which function as effective magnetic flux pinning centers in the range of the magnetizing field. The last is inconsistent with results of the polarized microscopy, which shows rather an increase of defects with lanthanum doping, however, it is in agreement with decrease of the average grain size, and of the first penetration magnetic field H_{pl}^{wl} for the highest La doping level x = 0.1. A detailed analysis of the shape of magnetization loops of the oxygen post-annealed samples shows that their properties are close to melt textured sample properties. It is strongly probable that this is caused by the existence of clusters of the connected grains with good current junction properties. So, La doping improves the superconducting properties of the grain connections at least for the lowest La content x = 0.04, while the higher content of the La leads to opposite effect. In addition, the sharp transition curves of the induced normalized voltage of the samples after the post-annealing in flowing oxygen show no shoulders up to 77 K and below (figure 1), which are considered to be fingerprints of sample inhomogeneity or oxygen non-stoichiometry. Unfortunately, we do not know the actual oxygen stoichiometry of our samples. However, the determination of oxygen in Tl based superconductors is highly dubious, since in the structure we have atoms which undergo oxidation and reduction (Tl). From the analysis of the $R(T)$ dependences of the samples it can be concluded, that while sintered samples are mostly slightly underdoped, oxygen annealed samples are in the almost optimally doped state showing mostly a linear $R(T)$ dependence. Therefore, it can be stated that post oxygen annealing leads to an almost optimal hole concentration, and so to higher values of critical temperature. It also improves the intergrain critical current density, as it follows from magnetization data. All the above facts suggest the possibility of a rather more complex behavior in (Tl,Pb)-superconductors doped with lanthanum.

CONCLUSIONS

The post oxygen annealing strongly improves the current properties of intergrain superconducting contacts and leads to a positive effect on the critical temperature T_c^{on} and the transition widths ΔT_c^{on}. The best values of ΔT_c^{on} ~119.5 K and ΔT_c^{on} ~0.8 K were obtained for the post-annealed samples with La-doping level x = 0.04. The powder diffraction data analysis proved that (Tl,Pb)-1223 is the dominant phase with volume fraction of more than 94 %. The La doping initiates a formation of the (Tl,Pb)-1212 phase and significantly decreases magnetization hysteresis. The intergrain critical current densities for higher lanthanum contents ($x \geq 0.07$) relative to parent samples decrease. The anomalous (positive) position of the central peak of the magnetization hysteresis loops in our bulk $(Tl_{0.6}Pb_{0.5})(Sr_{0.8}Ba_{0.2})_2Ca_2Cu_3O_{8+\delta}$ - x $LaO_{1.5}$ samples was observed for higher values of the magnetizing field. The 28 months ageing of the samples led to a relatively weak degradation of their j_c(H) dependences.

Acknowledgement

This work was supported by the Slovak Grant Agency for Science Project No. (2/4091/04), "High-Temperature Superconductors, Their Magnetic Properties, and Development of SQUID Magnetometric Methods". Authors express their thanks to Prof. G. Gritzner (J. Keppler University, Linz) for the provision of experimental facilities for the synthesis of the samples and his valuable advice.

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VLIV DODATEČNÉHO ŽÍHÁNÍ V KYSLÍKU A DOPOVÁNÍ LANTHANEM NA MEZI- A NITROZRNOVÉ VLASTNOSTI SUPRAVODIČŮ (Tl,Pb)-1223

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Byl zkoumán vliv žíhání v kyslíku a nízkoúrovňového dopování La^{3+} v systému (Tl,Pb)-1223. Vzorky s nominálním složením $(Tl_{0.6}Pb_{0.5})(Sr_{0.8}Ba_{0.2})_2Ca_2Cu_3O_{8+\delta}$ - x $LaO_{1.5}$, kde x je v rozmezí 0.00 až 0.10, jsme připravili metodou sol-gel. Zkoumali jsme jejich supravodivé mezi- a nitrozrnové vlastnosti, fázové složení a mikrostrukturu. Výsledky rtg difrakce ukázaly, že (Tl,Pb)-1223 je ve všech vzorcích hlavní fází. Dopování La vyvolává tvorbu fáze (Tl,Pb)-1212 a snižuje objemovou supravodivost. Dodatečné žíhání v kyslíku značně zlepšuje mezizrnové supravodivé spoje a má příznivý vliv na kritickou teplotu, T_c^{on} a ΔT_c^{on}. Pík ve středu hysterezní smyčky při intenzitě pole blízké nule je v nezvyklé kladné pozici na sestupné větvi vnějšího pole.