$SmBa_2Cu_3O_{7-\delta}$ ceramics processed under oxygen pressure of 250 bar: Enhancement of intragrain superconducting properties

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Polycrystalline samples of $SmBa_2Cu_3O_{7-\delta}$ have been processed under oxygen pressure of 250 bar. Several of their properties typical for highly oxygenated "123" phases were revealed: T_c=96 K as measured by ac magnetic susceptibility, high orthorhombic distortion of the unit cell, negative thermopower at room temperature, an exceptionally high specific-heat jump at T_c, highly irreversible magnetization at 4.2 K, and almost 100% diamagnetic signal at 77 K. Surprisingly, the value of electrical resistivity in the normal state and its temperature dependence were characteristic for semiconducting materials. The superconducting transition was observed as a sharp drop followed by a long tail, which was strongly dependent on the measuring current. Thus, $SmBa_2Cu_3O_{7-\delta}$ processed under an elevated oxygen pressure revealed intragrain properties similar to that of the best $YBa_2Cu_3O_{7-\delta}$ samples, however, poor intergrain electrical conductivity was observed.

INTRODUCTION

The structure and superconducting properties of fully oxidized $RBa_2Cu_3O_{7-\delta}$ compounds (R=Y or lanthanides except Ce, Pr, Tb) are very similar although a weak dependence of critical temperature T_c on the radius of the R ion has been reported.[1] Despite these similarities the important differences exist between compounds with larger R^{3+} ionic radius (La, Pr, Nd, Sm, Eu, Gd) and those with smaller R^{3+} ionic radius (Y and Dy, Ho, Er, Tm, Yb, Lu). The rare-earth ions from the first group are large enough to partially substitute on the Ba sites resulting in solid solutions with the general formula $R(Ba_{2-x}R_x)Cu_3O_y$.[2] In these solid solutions, the superconducting properties are degraded with increasing x. The tendency of substitution of Ba by R ions causes serious problems in obtaining phases with exact "123" cation stoichiometry. However, Wada *et al.*[3] reported successful preparation of $LaBa_2Cu_3O_7$ phase with zero resistance at 92 K avoiding substitution of La for Ba by annealing in nitrogen. Another difficulty in preparation of good quality samples of the $RBa_2Cu_3O_{7-\delta}$ compounds with larger R^{3+} ions is their higher sensitivity to the oxygen deficiency. As the ionic radius of the R^{3+} ion becomes larger, the falloff of T_c becomes more rapid with oxygen depletion and the oxygen stoichiometry, where superconductivity disappears, moves to higher values.[4–7] It is well established that the fully oxidized and good quality samples of $YBa_2Cu_3O_{7-\delta}$ possess not only the sharp superconducting transition above 90 K but also reveal negative thermopower, e.g., Ref. 8, and a distinct jump of the specific heat at T_c, e.g., Ref. 9. The last two features have not been reported so far for $RBa_2Cu_3O_{7-\delta}$ compounds with larger R^{3+} ions probably due to difficulties in obtaining samples with exact 123 stoichiometry and their higher sensitivity to oxygen deficiency.

Recently, it has been shown that the T_c of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ ($0.1 \leq x \leq 0.6$) could be increased by synthesizing and annealing the compound under high oxygen pressure.[10,11] These results stimulated us to apply similar high pressure treatment to $SmBa_2Cu_3O_{7-\delta}$ with exact 123 cation stoichiometry, as a member of $RBa_2Cu_3O_{7-\delta}$ family with large R^{3+} ionic radius. In this work we present the results of electrical resistivity, ac and dc magnetic susceptibility, thermopower and specific heat measurements for two $SmBa_2Cu_3O_{7-\delta}$ samples, differently processed under elevated pressure of oxygen.

EXPERIMENT

Samples of $SmBa_2Cu_3O_y$ were prepared by the conventional solid state reaction. Stoichiometric quantities of $BaCO_3$ (spectroscopically pure), Sm_2O_3 (99.9%), and CuO (99.99%) were thoroughly mixed in an agate mortar and pestle, placed into alumina crucibles and calcined at 900 °C overnight. Subsequently, the mixture was regrounded, pressed into pellets and sintered at 930 °C for several days with intermediate grindings. The obtained samples were heated at 800 °C in flowing oxygen for 5 h, followed by slow (15 °C/h) cooling to room temperature. This sample will be then named as LP-$SmBa_2Cu_3O_{7-\delta}$.

Few pellets of LP-$SmBa_2Cu_3O_{7-\delta}$ were annealed in a closed reaction tube in pure oxygen under pressure of 250 bar (as measured at 450 °C) in a Morris Research HPS-5015E furnace. First sample (HP1-$SmBa_2Cu_3O_{7-\delta}$) was processed by 40 h annealing at 450 °C followed by furnace cooling. The second sample (HP2-$SmBa_2Cu_3O_{7-\delta}$) was processed in a more complicated procedure: 2 h at 500 °C, 18 h at 450 °C, 20 h at 400 °C, 24 h at 350 °C, and then furnace cooled. The cooling rate between the temperature steps was 0.1 K/min.

The phase composition and lattice parameters were determined by x-ray powder diffraction using Cu K_α radiation. Microscopic observations of samples were performed on fractured surfaces using a Philips SM-515 scanning electron microscope (SEM) equipped with an energy dispersive x-ray (EDX) spectrometer. The average copper valence V_{Cu} was determined by the iodometric titration method proposed by Nazzal *et al.*[12] The oxygen content ($7-\delta$) was then calculated using charge neutrality (assuming that the cation stoichiometry was known).

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TABLE I. The lattice parameters, a, b, and c, orthorhombicity parameter $(b-a)/(a+b)$, as well as the oxygen content $(7-\delta)$ for initial (LP) and for two processed under elevated pressure of oxygen (HP1, HP2) $SmBa_2Cu_3O_{7-\delta}$ samples.

Sample	a [Å]	b [Å]	c [Å]	$(b-a)/(a+b)$ [%]	$7-\delta$
LP	3.846	3.911	11.730	0.84	6.95±0.05
HP1	3.845	3.907	11.727	0.80	6.90±0.05
HP2	3.845	3.910	11.721	0.84	7.00±0.05

ac magnetic susceptibility was measured using Lake Shore 7000 susceptometer in the ac field of 10 Oe and frequency 111.1 Hz. dc magnetization measurements in superconducting state were performed at 4.2 K in magnetic field oriented parallel to long dimension of the cylindrical sample.

The thermopower (S) was measured in the temperature range 4.2–300 K using a differential technique in helium gas with respect to two copper blocks. The absolute accuracy averaged 15%, as confirmed by a pure Pb standard. A quality of thermal contacts between the blocks and the sample was proved by electrical resistance measurements, which was no higher than few ohms in the whole temperature range. Each sample was measured several times in different directions and at different places on sample surfaces, showing a results scatter of the order ± 1 μV/K at room temperature.

The specific heat measurements were carried out in the automated adiabatic calorimeter as depicted in Ref. 13. The sample was located on a flat holder of the heat capacity equivalent to ~200 mg Cu at the room temperature and glued by a weighted amount of Apiezon T grease and aluminium powder mixture. Two independent adiabatic screens were used to minimize energy exchange with the surrounding. The calorimeter operation is alternatively combining two different modes: a heat pulse method with better absolute accuracy and a faster continuous method with better resolution. The typical heating rate for both methods is 5–10 mK/s. The mass of samples varied around 500 mg.

The resistivity (ρ) measurements were performed by standard four-probe method in the temperature range 4.2–300 K. The samples were cut from the pellets into the shape of bars of $\sim 8\times 1\times 1$ mm^3.

RESULTS AND DISCUSSION

Powder x-ray-diffraction analysis indicated that all obtained $SmBa_2Cu_3O_{7-\delta}$ samples (LP, HP1, and HP2) were single phase. However, small amounts of $BaCuO_2$ phase were detected during SEM observations. The lattice parameters and the oxygen content for all samples are presented in Table I. All samples revealed high oxygen content and high orthorhombic distortion $(b-a)/(a+b)$, with respect to $SmBa_2Cu_3O_{7-\delta}$ samples prepared by other authors.[14] It is interesting to note that even after processing under elevated oxygen pressure the oxygen content did not exceed the value of 7.

The real χ' and the imaginary χ'' parts of ac magnetic susceptibility for the as-prepared LP and two processed at elevated oxygen pressure $SmBa_2Cu_3O_{7-\delta}$ samples, HP1 and HP2, in the vicinity of the superconducting transition are shown in Fig. 1. It is seen that for HP2 sample the superconducting transition is very sharp with an onset at temperature about 96.0 K. This is one of the highest critical temperatures found for 123 type family. This result confirms earlier observations that T_c of $RBa_2Cu_3O_{7-\delta}$ phases increases with increasing ionic radius of R^{3+}.[1,15,16] The behavior of imaginary part of susceptibility is rather unusual. The behavior of χ'' for as-prepared LP sample is characteristic for all ceramic compounds. There is a rather sharp peak connected with ac losses

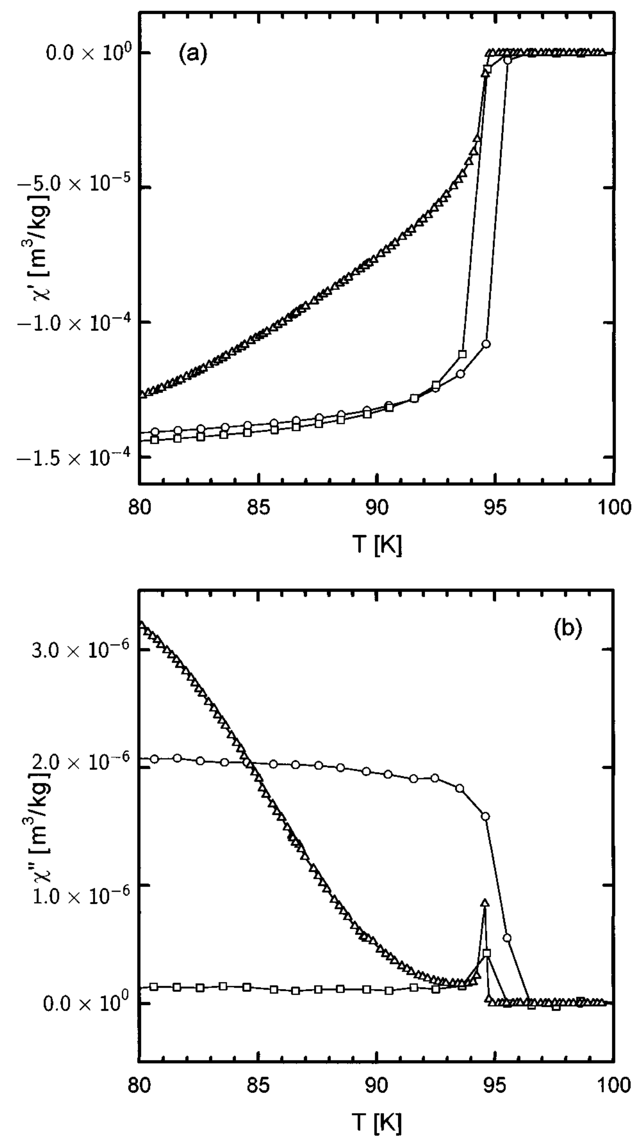

FIG. 1. The real χ' (a) and the imaginary χ'' (b) part of ac magnetic susceptibility in the vicinity of the superconducting transition for $SmBa_2Cu_3O_{7-\delta}$. Symbols denote (△) the initial LP sample, and (□) HP1, and (○) HP2, the two samples processed under elevated pressure of oxygen.

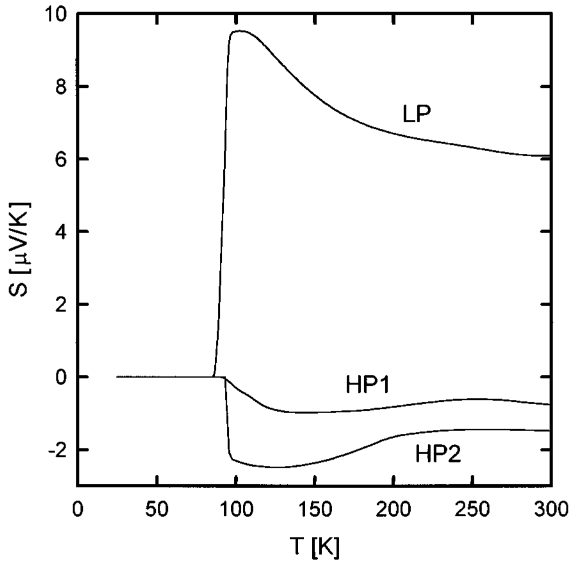

FIG. 2. The temperature dependence of the thermopower S for $SmBa_2Cu_3O_{7-\delta}$: LP—the initial sample; HP1 and HP2—two samples processed under elevated pressure of oxygen.

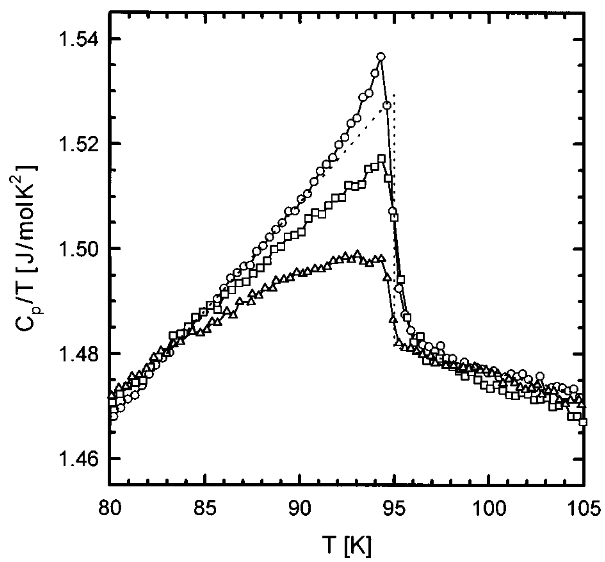

FIG. 3. The specific heat over temperature C_p/T for $SmBa_2Cu_3O_{7-\delta}$ in the vicinity of superconducting temperature. Symbols denote (△) the initial LP sample, and (□) HP1 and (○) HP2, the two samples processed under elevated pressure of oxygen. The dotted line shows the entropy-conserving construction used for estimating the specific heat jump at T_c for the HP2 sample.

inside the grains and a broad maximum ascribed to intergranular losses. For the sample HP1, it is seen that the grains are almost completely decoupled and intergranular losses are close to zero. Quite unsuspected is the behavior of χ'' for HP2 sample, which strongly increases at T_c and remains constant down to 4.2 K. We are not able now to explain such a behavior.

The temperature dependences of the thermopower, $S(T)$, for the three $SmBa_2Cu_3O_{7-\delta}$ samples, LP, HP1, and HP2, are shown in Fig. 2. The $S(T)$ for LP-$SmBa_2Cu_3O_{7-\delta}$ sample is typical as for $YBa_2Cu_3O_{7-\delta}$ compound with oxygen deficiency of $\delta \approx 0.20$.[17] For the both HP-$SmBa_2Cu_3O_{7-\delta}$ samples the thermopower is negative and weakly depends on temperature; similar behavior has been observed for $YBa_2Cu_3O_{7-\delta}$ polycrystalline samples[8,18–20] and crystals in ab plane,[19,21] when δ is below 0.05. According to our knowledge, up to now, negative values of thermopower have never been observed for 123 compounds with rare earths with large ionic R^{3+} radius, like Sm (the lowest, but positive value of S for $SmBa_2Cu_3O_{7-\delta}$ was reported in Ref. 22).

dc magnetization measurements for HP2-$SmBa_2Cu_3O_{7-\delta}$ in low magnetic field up to 100 Oe showed the shielding of magnetic flux at 77 K corresponding to 90–100 % of perfect diamagnetism. The critical current density j_c for HP2 sample was determined from irreversible magnetization loop using the critical state equation in Bean model[23] j_c [A/cm^2] $=30\Delta M/d$, where ΔM [emu/cm^3] is the width of the magnetization loop and d [cm] is a characteristic transverse dimension, here the average diameter of grain assessed from SEM images. The value of critical current density is estimated to be j_c (T=4.2 K, B=0.5 T)=(4–8)$\times 10^6$ A/cm^2. This high value corresponds to j_c for polycrystalline samples and thin films of $YBa_2Cu_3O_{7-\delta}$,[24,25] with high oxygen concentration ($\delta \leqslant 0.05$).

The specific heat over temperature C_p/T versus temperature in the vicinity of superconducting transition is presented in Fig. 3. The entropy-conserving construction was used for determination of the height of the specific heat jumps. The dotted line in Fig. 3 shows an example of this construction for HP2 sample. A clear upturn of C_p/T near the middle of the transition with respect to the straight lines extrapolated from temperatures off the middle is probably connected with superconducting fluctuations. The values of ΔC_p and of thermopower at room temperature S_{300}, which are summarized in Table II, locates well all, i.e., LP, HP1, and HP2, samples in the mutual S_{300} versus ΔC_p linear dependence reported in our previous work[26] for 90 K 123 samples. Up to now, only few authors reported the observation of the weak specific heat anomaly at T_c for the 123 compounds from the group with larger R^{3+} ionic radius, i.e., with Sm,[27] with Eu,[28] and with Gd.[29,30] The pronounced jump in $C_p(T)$ at T_c for HP2 sample, which is a member of this group, is of the height comparable with the best $YBa_2Cu_3O_{7-\delta}$ samples.

All data described above indicate that the annealing of $SmBa_2Cu_3O_{7-\delta}$ compound under elevated oxygen pressure at temperature ~400 °C lead to significant improvement of its superconducting and transport properties. Nevertheless,

TABLE II. The ρ_{300}, S_{300}, and ΔC_p for initial (LP) and for two processed under elevated pressure of oxygen (HP1, HP2) $SmBa_2Cu_3O_{7-\delta}$ samples.

Sample	ρ_{300} [m Ω cm]	S_{300} [μV/K]	ΔC_p [J/mol K]
LP	2.5	6.1±1	1.6
HP1	14	−0.8±1	3.6
HP2	15	−1.5±1	4.6

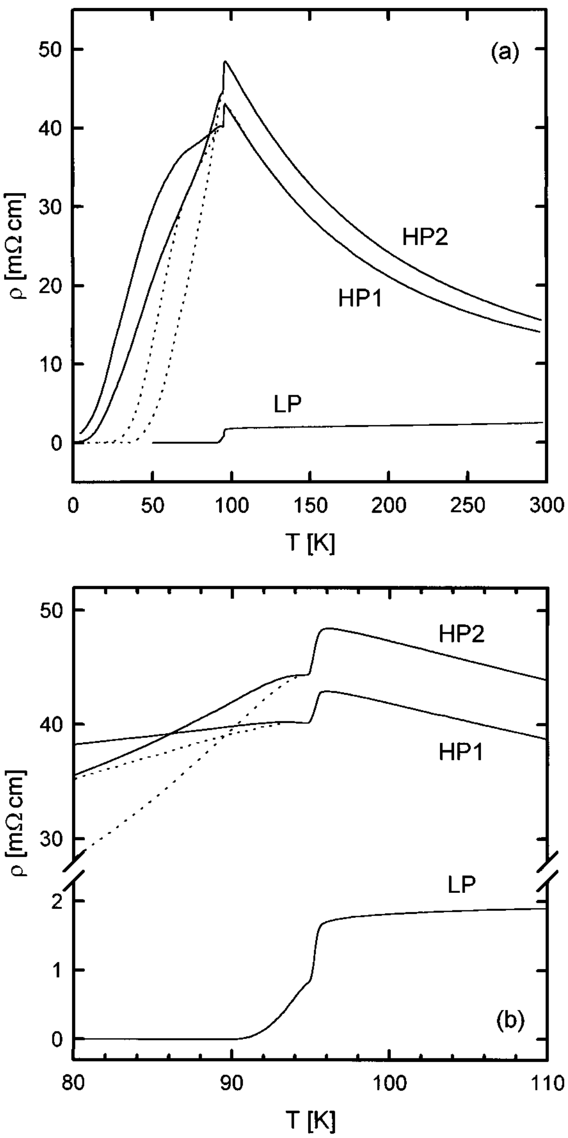

FIG. 4. The temperature dependence of electrical resistivity ρ for $SmBa_2Cu_3O_{7-\delta}$: LP—the initial sample; HP1 and HP2—two samples processed under elevated pressure of oxygen: (a) the whole temperature range and (b) the vicinity of the superconducting transition. The solid and dotted lines denote the ρ measurement with current of 1 and 0.1 mA, respectively.

the electrical resistivity ρ changed in a quite different manner. Figure 4(a) presents the temperature dependence of ρ of the three $SmBa_2Cu_3O_{7-\delta}$ samples. The relatively low room temperature value of $\rho(300\ \mathrm{K})\approx 2.5$ m Ω cm with respect to other polycrystalline 123 samples[26] and the linear temperature dependence indicate a good quality of the initial LP sample. As seen in the Fig. 4(b), a sharp drop at 95 K occurs, followed by a longer tail. The zero resistivity is reached at about 90 K. However, the room temperature value of the thermopower $S(300\ \mathrm{K})=6.1\pm 1$ μV/K locates this sample near the edge of the 90 K plateau.[26] A drastic change in comparison to LP sample is observed for both HP samples. The very high value of $\rho(300\ \mathrm{K})\approx 14$ and 15 m Ω cm, for HP1 and HP2 samples, respectively, the semiconductorlike temperature dependence above T_c and very long, strongly dependent on the measurement current tails below T_c were observed. Nevertheless, the sharp drops in $\rho(T)$ were observed for the same temperature $T_c=95$ K as for the LP initial sample. This behavior of $\rho(T)$ suggests that oxidizing process at elevated pressure causes worsening of the electrical contacts between the grains. We would like to underline that the HP samples did not become brittle, so that the explanation of the poor contacts by just space separation of grains seems less probable. The possible reason might be the $BaCuO_2$ phase precipitated on the grain boundaries, as seen on SEM picture in Fig. 5; however, other mechanism of the grains boundaries degradation cannot be ruled out.

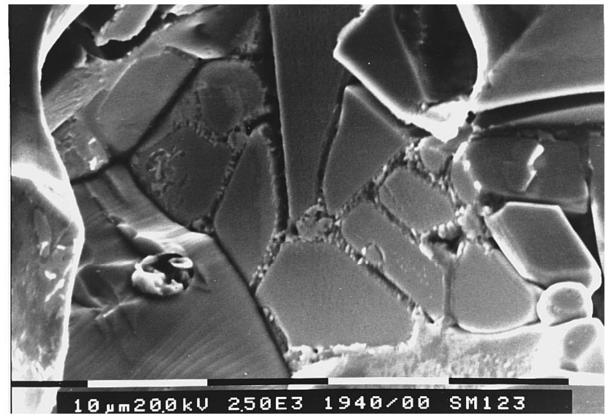

FIG. 5. SEM picture of the HP1-$SmBa_2Cu_3O_{7-\delta}$ sample fractured surface. Between the grains the $BaCuO_2$ phase is visible.

CONCLUSIONS

A $SmBa_2Cu_3O_{7-\delta}$ compound from the family of 123 phases with large R^{3+} ionic radius has been obtained using elevated oxygen pressure processing. Its superconducting parameters were of the quality, which, up to now, were observed only for 123 compounds with smaller R^{3+} ionic radius. Namely, for our HP-$SmBa_2Cu_3O_{7-\delta}$ samples we observed $T_c=95$ K (from ac susceptibility measurements even $T_c=96$ K for HP2 sample), which is one of the highest critical temperatures observed in 123 family. Moreover, we observed the high orthorhombic distortion of the unit cell, and for HP2 sample: the negative value of thermopower, exceptionally high specific heat jump at T_c, almost 100% of diamagnetic signal at 77 K, and highly irreversible magnetization at 4.2 K, i.e., large critical current. In our previous work[26] we revealed a mutual, linear S versus ΔC_p dependence for 90 K 123 samples. The data from this paper shows that this relation might be observed even for the same sample, subsequently processed in different conditions.

Despite all the above, the temperature dependence of the electrical resistivity is very peculiar. In contrast to the all 90 K 123 superconductors, including the initial LP-$SmBa_2Cu_3O_{7-\delta}$ sample, the HP1- and HP2-$SmBa_2Cu_3O_{7-\delta}$ samples revealed high resistivity value at room temperature and the semiconductorlike $\rho(T)$ dependence. The superconducting transition was observed as a sharp drop at 95 K followed by a very long tail, strongly dependent on the measurement current. These $\rho(T)$ dependences indicates that the elevated oxygen pressure processing of $SmBa_2Cu_3O_{7-\delta}$ samples resulted in degradation of grain boundaries. The question whether this degradation is an inherent feature of samples of high-T_c superconductors treated this way is still open and further studies are needed.

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