



Influence of Heat Treatment at 550–810°C on Inter- and Intragrain Critical Currents of Bi,Pb-2223 Ceramics

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Abstract. The degradation of the superconducting phase $\text{Bi}_{1.65}\text{Pb}_{0.35}\text{Sr}_{1.8}\text{Ca}_{2.2}\text{Cu}_3\text{O}_y$ and its characteristics: electrical resistivity R , critical temperature T_c ($R=0$), critical current density j_c , and volume fraction of Meissner phase C_m , have been investigated at 550–810°C and $P_{\text{O}_2}=2 \cdot 10^1 \dots 1 \cdot 10^5$ Pa by X-ray diffraction, resistance, inductance and magnetic methods. It was established that at $P_{\text{O}_2} \geq 10^3$ Pa degradation of the ceramic samples runs through the solid solutions decomposition. As a result, the intergrain critical current is decreased 10–20 times while the intragrain one is increased 1.5–2 times. At $P_{\text{O}_2} = 10^1 - 10^2$ Pa the inter- and intragrain critical currents are decreased by 5–10 times and by 1.5–2 times respectively as a result of oxygen extraction without visible destruction of the Bi,Pb-2223 structure.

Keywords: high T_c superconductor, critical currents, superconductivity degradation, oxygen-stoichiometry, (Bi, Pb-2223) ceramics

1. Introduction

The superconducting phase $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (Bi,Pb-2223) with the highest critical temperature 105–110 K is not stable at temperatures between 500–800°C in air and oxygen. It is decomposed with the partial or total degradation of transport critical currents in the ceramic samples [1,2]. In nitrogen ($P_{\text{O}_2}=20-50$ Pa) the crystal structure of the phase Bi,Pb-2223 is stable up to temperatures about 750°C [3] while the critical parameters degrade partially without visible destructions of the superconducting phase crystal structure [4,5]. These results indicate different mechanisms of the superconductivity degradation at high and low partial pressures of oxygen.

This investigation on the determination of the critical parameter degradations of the superconducting Bi,Pb-2223 ceramics in a wide range of the oxygen partial pressure $2 \cdot 10^1 \dots 1 \cdot 10^5$ Pa was carried out to evaluate the principal essence of the indicated degradation mechanisms and their dominant action fields. At-

tention was primarily paid to the intergrain critical current density as the most sensitive structural characteristic of the ceramic HTSC. For comparison, the intragrain critical current density was also determined in the initial ceramic samples and after their partial degradation by annealing in air and nitrogen at 700°C during 8 hours.

2. Experiment

The main part of this research is carried out on the ceramic samples of the nominal composition $\text{Bi}_{1.65}\text{Pb}_{0.35}\text{Sr}_{1.8}\text{Ca}_{2.2}\text{Cu}_3\text{O}_y$. Basically, the same results were also obtained on the samples of the initial compositions $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ and $\text{Bi}_{1.65}\text{Pb}_{0.35}\text{Sr}_{1.9}\text{Ca}_{2.1}\text{Cu}_3\text{O}_y$. On the X-ray diffraction pattern the initial ceramic samples were near single phase, their density was about 90%. The superconducting volume fraction was registered at 75–90% depending on the heat treatment and cooling conditions of the samples. The electrical resistivity, critical parameters were determined

by 4-probe resistive measurements on DC current as described in [2]. The critical parameters were determined by magnetic susceptibility measurements on bar-shaped samples with cross section about 1 mm² located along the AC-magnetic field of 10 Oe as well as on powders in 100 Oe AC-magnetic field too. Imaginary part of the AC susceptibility was used to estimate j_c , as described in [6]. Bean's model of flux penetration in a slab or cylinder was applied. For the ceramics samples, the single peak on $\chi''(T)$ -curve was assumed to correspond to intergrain currents (j_{cb}), which was supported by the nearly full shielding at low temperatures, while for powders, the $\chi''(T)$ peak was assigned to intragrain currents (j_{cg}). The slab thickness was used as characteristic size to derive j_{cb} , and average grain size of 10 microns—to estimate j_{cg} . The error of T_c measurements was 1 K. The errors of j_{cb} and j_{cg} measurements were about 20% and 50% respectively.

The j_c , determined by resistive method was measured at 77 K in zero magnetic field. The voltage criterion was 1 μ B.

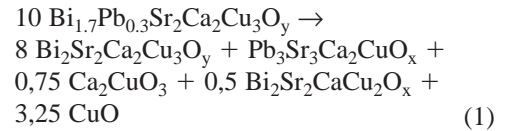
3. Results and Discussion

The data j_c , R (at room temperature, R_r), T_c ($R=0$) given in Figs. 1 to 4, table 1, were measured by the resistive method. The critical current in this case depends on the intergranular states and may be identified as intergrain current density.

The degradation of critical current density j_c (77K),

critical temperature T_c ($R=0$) and changes of resistance R at room temperature (R_r) of the ceramic samples after annealing in air at 750°C are shown in Fig.1. It is possible to see that curves of T_c and j_c for the samples quenched from temperatures of 820–840°C pass through the maximum (curves 1,3). On the contrary, the samples cooled slowly from 820–840°C when the electric furnace was turned off have shown the increase of T_c on 2–3 K and j_c by 1.5–2 times ($t=0$) and a smooth shape of the degradation kinetic curves (curves 2,4).

According to data of X-ray diffraction, C_m , j_c at 810°C; the superconducting phase was not degraded any more and the degradation rate was quickly decreased when the temperature went down below 600°C (Fig 2). The main product of the decomposition was the 2223 phase without or with small content of Pb. The dominant impurity was the phase of the $Pb_3(Sr,Ca)_5CuO_y$ kind [7]. There also could be found smaller contents of the phase impurities like Bi-2212, Bi-2201, Ca_2CuO_3 and apparently CuO. Therefore the degradation process of Bi,Pb-2223 can be approximately described by the following reaction, for example:



The same phases were also observed after degradation in oxygen. In addition phase the SrPbO_3 was found sometimes. In the decomposition products at

Table 1. Meissner phase C_m (vol.%), critical temperature T_c ($R=0$)(K) and critical current density j_c (77 K, OT) (A/cm²) of ceramic samples $\text{Bi}_{1.65}\text{Pb}_{0.35}\text{Sr}_{1.8}\text{Ca}_{2.2}\text{Cu}_3\text{O}_y$ before and after annealing at 700°C in He, contained 8; 0.69; 0.17 vol.% O_2 and after the following reannealing at 400°C 1,5 h. in air.

O_2 in He vol%	Parameter s	Annealing at 700°C, hours			Reannealing at 400°C 1,5 h, air
		0	2.5	40.5	
8	C_m	78	50	27	27
	T_c	105	105	105	105
	J_c	1200–1400	940–1000	100–150	150–200
0.69	C_m	78	51	37	37
	T_c	107	106	106	106
	J_c	1200–1400	900–1100	600–700	1100–1250
0.17	C_m	78	50	43	44
	T_c	102	101	100	101
	J_c	1200–1400	1000–1100	360–450	900–1000

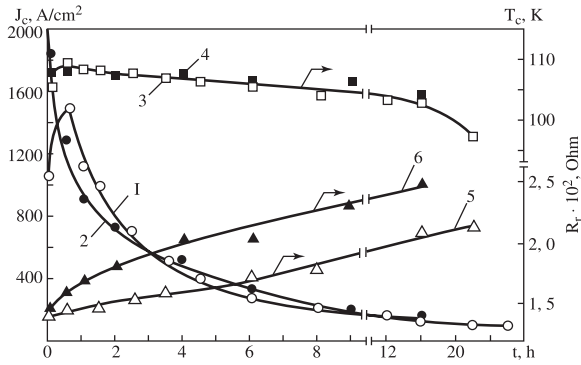


Fig. 1. Changes of j_c (77 K) (1,2), T_c (3,4) and R_r (5,6) in quenched (1,3,5) and slowly cooled (2,4,6) from 840°C ceramic samples of $Bi_{1.65}Pb_{0.35}Sr_{1.9}Ca_{2.1}Cu_3O_y$ after annealing in air at 750°C.

high pressures of oxygen this phase was dominant [1]. The degradation rate in oxygen was 2–3 times higher than that in air. The non-single phase samples of nominal composition $Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_y$ were degraded more actively up to total loss of superconductivity at 77 K.

The superconducting phase and its properties in partially degraded samples were already restored on 60–80% during 3–4 hours at 810°C, during 0.5–1 hour at 830°C. Then there were practically no further changes, though the superconducting volume fraction raised slowly [2]. Practically complete recovery of the superconducting phase volume fraction and its param-

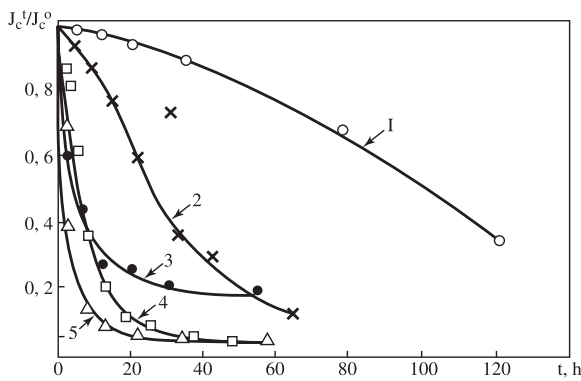


Fig. 2. Dependencies of j_c'/j_c^o —critical current density (77 K) of the samples before annealing, j_c' (77 K)—after annealing t hours, A/cm^2 vs annealing duration (t) of the $Bi_{1.65}Pb_{0.35}Sr_{1.9}Ca_{2.1}Cu_3O_y$ ceramic samples in air at temperatures (°C): 600(1), 650(2), 790(3), 700(4), 775(5).

eters required longer firing in air at 850–855°C during 40–50 hours.

In nitrogen ($P_{O_2}=20$ Pa), at temperatures of 550–750°C; the superconducting characteristics were decreased, the resistance was increased during the first 20–40 minutes and they were practically not changed during the following 10–20 hours (Fig. 3). On the X-ray diffraction, the phase composition was not changed noticeably. The recovery of superconducting parameters up to 80–90% took place at 300–400°C in air, but the superconducting volume fraction was not changed. These data indicate that the Bi,Pb-2223 superconductivity degradation in nitrogen from resulted oxygen extraction without visible phase decomposition.

The degradation of Bi,Pb-2223 ceramic samples was studied in addition at 700°C in helium with intermediate amounts of oxygen 8; 0,69 and 0,17 vol.%. As it is possible to see from Fig. 4 and table 1 the maxi-

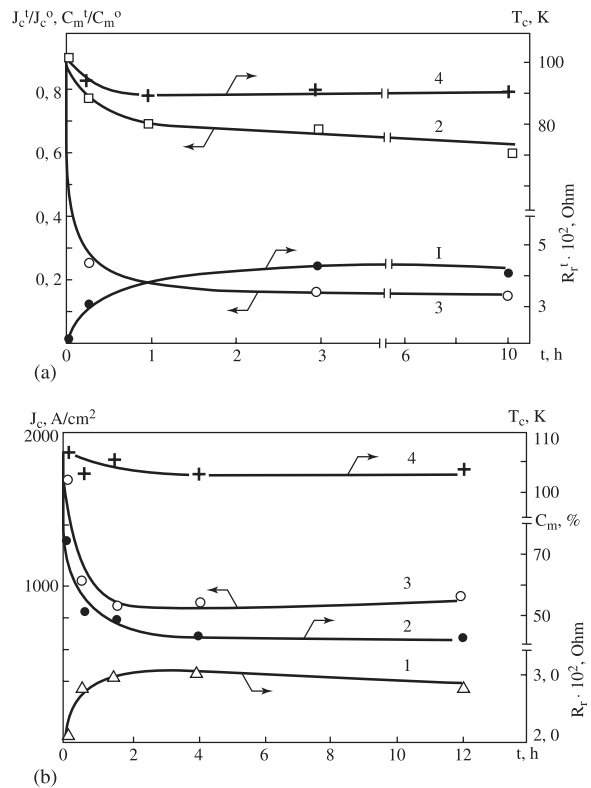


Fig. 3. Changes of R_r (1), C_m' C_m'/C_m^o (2), j_c , j_c'/j_c^o (3), T_c (4) in $Bi_{1.65}Pb_{0.35}Sr_{1.8}Ca_{2.2}Cu_3O_y$ samples after annealing in N_2 at 550°C (a) and 750°C (b).

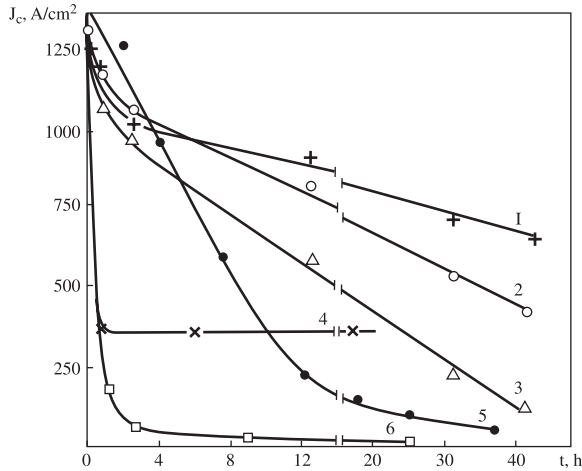


Fig. 4. Changes of Bi_{1.65}Pb_{0.35}Sr_{1.8}Ca_{2.2}Cu₃O_y ceramic samples critical current densities j_c (77 K), after annealing at 700°C at P_o (Pa): 6,9·10²(1); 1,7·10²(2); 8·10³(3); 2·10⁴(4); 2,1·10⁴(5); 1·10⁵(6).

imum stability of critical current took place at 0,69 vol.% O₂ in the gas phase. The following heat treatment at 400°C in air showed the recovery of the critical currents up to 80–90% in the ceramic samples after their degradation at 700°C in the gas phases with 0.17 and 0.69 vol.% O₂. This parameter was not changed noticeably in the samples decomposed in the gas phase with 8 vol.% O₂ (Table 1). Thus, at P_{O_2} higher than ~ 1.10³ Pa, the superconductivity degradation at 550–800°C is caused by the Bi,Pb-2223 decomposition and at the lower P_{O_2} (10–10²Pa) the superconductivity degradation at 550–750°C dominates because of the oxygen extraction from the Bi,Pb-2223 phase without its visible decomposition.

In order to compare changes of the inter- and intragrain critical currents at degradation of supercon-

ductivity at high and low P_{O_2} the method of magnetic susceptibility measurements has been used. The results are shown in the Table 2. It is possible to see that the intergrain critical currents (j_{cb}) are decreased when samples are annealed in air and nitrogen at 700°C. However the intragrain critical current (J_{cg}) was increased by 1.5–2 times at partial decomposition of the 2223 phase in air, the critical temperature remaining almost unchanged. In nitrogen the intragrain critical current was decreased 1.5–2 times, as result of oxygen extraction.

The temperature dependence of the inter- and intragrain critical currents were in accordance with the correlation [8].

$$j_{cb}(j_{cg}) \sim (1 - T/T_c)^n \quad (2)$$

The parameters n are shown in the Table 2. The mean n value for the intragrain critical currents is near 2 as well as for Bi,Pb-2212 and Bi,Pb-2223 whiskers [8]. This n value is typical for the SNS as well as for the SIS Josephson junctions near the critical temperature [8]. The n value for the intergrain critical currents were a little higher (Table 2). This indicate the more complete correlations on grain boundaries.

The character of j_{cb} changes depending on treatment conditions, determined by the method of magnetic susceptibility measurements, was identical to j_c (j_{cb}) changes, obtained by resistive method.

4. Conclusion

The superconducting properties of (Bi,Pb)₂(Sr,Ca)₄Cu₃O_y (2223) ceramics were degraded at the temperatures of 550-800°C and at the oxygen partial pressures of 10¹ . . . 10⁵ Pa. At $P_{O_2} \geq 10^3$ Pa, the degradation was carried out by the decomposi-

Table 2. Intergranular j_{cb} , intragranular j_{cg} critical current density (A/cm²), critical temperature T_c (K) by susceptibility measurements, n from correlations $j_{cb}(j_{cg}) \sim (T_c - T)^n$ in initial Bi_{1.65}Pb_{0.35}Sr_{1.8}Ca_{2.2}Cu₃O_y samples and after their annealing at 700°C 8 hours in air and nitrogen.

Annealing T,K	Initial samples		700°C, 8 h, air		700°C, 8 h, N2	
	j_{cb}	j_{cg}	j_{cb}	j_{cg}	j_{cb}	j_{cg}
100	98	42300	8	28000	7	15000
90	670	150000	51	190000	74	73000
77	2500	350000	180	570000	400	200000
60	5900	—	623	—	1360	—
T_c ,K	110,2	—	110,6	—	108,9	—
n	2,57	1,73	2,65	2,48	3,28	2,21

tion of the 2223 phase to Bi-2212, Bi-2201, Ca_2CuO_3 and CuO phases. The highest degradation of the intergrain critical current density j_{cb} (77 K) up to its full loss took place after calcination at 700–775°C during 10–15 hours in air. The intragrain critical current j_{cg} (77 K) was increased also by 1.5–2 times even in the ceramics samples with full degradation of the intergrain critical current. At $P_{\text{O}_2} = 10^1 - 10^2$ Pa and at 550–750°C, the inter- and intragrain critical currents were degraded by 5–10 times and 1.5–2 times respectively as a result of an oxygen extraction without visible destruction of 2223 structure. Consequently for increasing of the critical currents the 2223 ceramics must be cooled slowly (200–300°C/h) from 800–860°C in air. The tempered ceramics must be heated 10–15 minutes at 700–750°C in air.

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