High-T_c superconductivity in the T1–Ba–Ca–Cu–O ceramic

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The results of an experimental study of high-T_c superconductivity of the ceramic $Tl_{1.4}BaCaCu_{1.5}O_y$, synthesized under various conditions, are stable and reproducible. The highest critical temperature obtained by us for this system is $T_c^0 = 125.3$ K.

After the pioneering work of Michel *et al.*[1] who discovered, for the ceramic $Sr_2Bi_2Cu_2O_7$, a new class of high-T_c superconductors with $T_c \approx 22$ K, which do not contain rare-earth elements, a vigorous search for new high-T_c superconductors is continuing. Thallium ceramics Tl–Ba–Cu–O and Tl–Ba–Ca–Cu–O, which were synthesized, with the exception of those obtained in Ref. 5, on the basis of the melt-(solid phase) reactions and annealed in oxygen were studied in Refs. 2–5. In the case of a multiphase ceramic Tl–Ba–Cu–O the superconducting transition occurs at $T_c^N = 90$ K and $T_c^0 = 81$ K. Two superconducting phases $Tl_2Ca_2Ba_2Cu_3$ (2223) and $Tl_2CaBa_2Cu_2O_7$ (2122) with $T_c^N \approx = 120$ K and $T_c^0 \approx 100$ K were identified in Ref. 3. The presence of the (2122) phase with $T_c^0 \approx 100$ K was confirmed in Ref. 4, as was the "zero"-resistance state at $T_c^0 = 120$ K for the single-phase superconducting ceramic $TlBaCaCu_2O_y$ with a tetragonal structure with $a = b = 3.841$ Å and $c = 19.77$ Å.

We have synthesized a high-T_c superconducting thallium ceramic by sintering a mixture of pressed powders Tl_2O_3, $BaCO_3$, $CaCO_3$, and CuO[6] in stoichiometric ratio obtained according to the formula $Tl_{1.4}BaCaCu_{1.5}O_y$. Some of the samples were obtained by sintering them at temperatures $T_s = 810$–870 °C for 1–10 h. Other samples were obtained by double sintering: after synthesizing the samples they were ground, pressed into pellets and sintered again.

X-ray diffraction analysis of the synthesized samples was carried out in a monochromatized Cu$K\alpha$ radiation. Figure 1 shows a typical spectrum of a superconducting thallium ceramic. This spectrum was identified on the assumption that the unit cell is a pseudotetragonal unit cell with $a = 5.43 \pm 0.01$ Å and $c = 29.6 \pm 0.1$ Å, in agreement with the data of Ref. 3. Under certain conditions of the synthesis yet another superconducting phase with $a = 5.41 \pm 0.01$ Å, $b = 5.43 \pm 0.01$ Å, and $c = 31.7 \pm 0.1$ Å was formed. The bulk nature of the superconductivity of the thallium ceramic was determined by an inductive method by placing the samples in the ~30-Oe magnetic field of the coil. The results of measurement of the Meisser effect for samples synthesized on the basis of a single-stage technology are compared in Fig. 2a. A weak but clearly distinguishable Meissner signal was detected at 126.5 K (sample 1) and at

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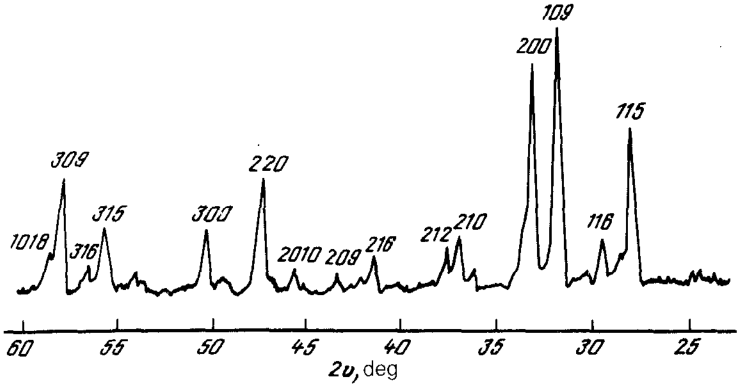

FIG. 1.

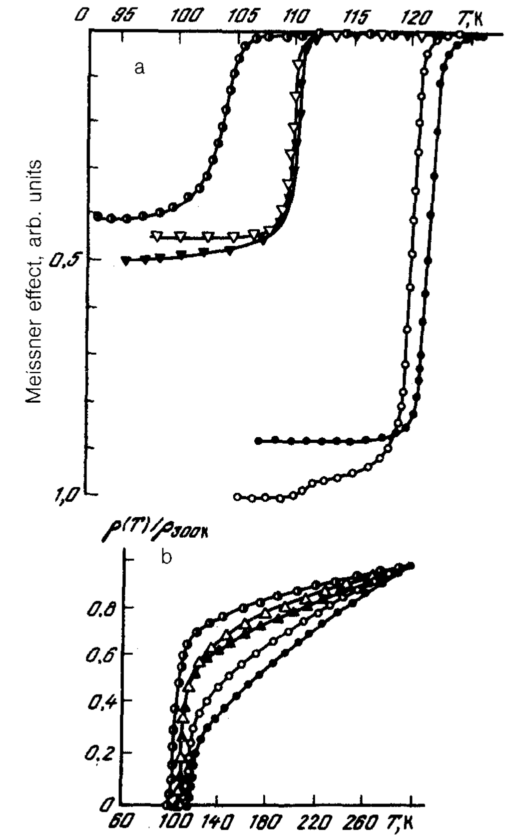

FIG. 2. Temperature dependence of the Meissner signal (a) and of the resistivity (b) of the $Tl_{1.4}BaCaCu_{1.5}O_y$ samples obtained by a single-stage method. ●—Sample 1; ○—sample 2; ▲—sample 3; △—sample 4; ◑—sample 5.

~ 125.5 K (sample 2). While the curve for the first sample flattens out at 119.5 K, the last sample reveals the presence of yet another superconducting phase near ~ 112 K. Samples 3 and 4 are similar in terms of their inductive characteristics. Nucleation of the superconducting phase in them occurs at ~ 123 K. The superconducting transition of sample 5, which begins at ~ 114 K, is broader than that of the other samples. Samples 1 and 2, which were synthesized at 870 °C for 20 min, 860 °C for 5 h, and 860 °C for 5 h, respectively, have the largest volume V_{ph} of the superconducting phase. The volume V_{ph} of the other three samples is half that of samples 1 and 2.

We conclude from the resistive characteristics of single-stage thallium samples (Fig. 2b) that the highest transition temperatures are $T_c^0 = 117$ K (sample 1) and 112.6 K (sample 2). Sample 5 has the lowest transition temperature, $T_c^0 = 99$ K. At 300 K the resistivity of these samples is in the range 5–1.2 m $\Omega \cdot$cm, which is comparable with the value of ρ300 K for $YBa_2Cu_3O_y$ samples of ordinary quality, suggesting that most of the test samples have extrinsic phases. It should be noted that at high temperatures the $\rho(T)$ curve of nearly all samples is no longer linear. Analysis of the data obtained by us shows that the samples synthesized at $T_s = 860$–870 °C for 5 h have high values of T_c^0 and V_{ph}. Holding the samples at $T_s = 850$ °C for 10 h or 1 h resulted in lower values of T_c^0 and V_{ph} (samples 3 and 4).

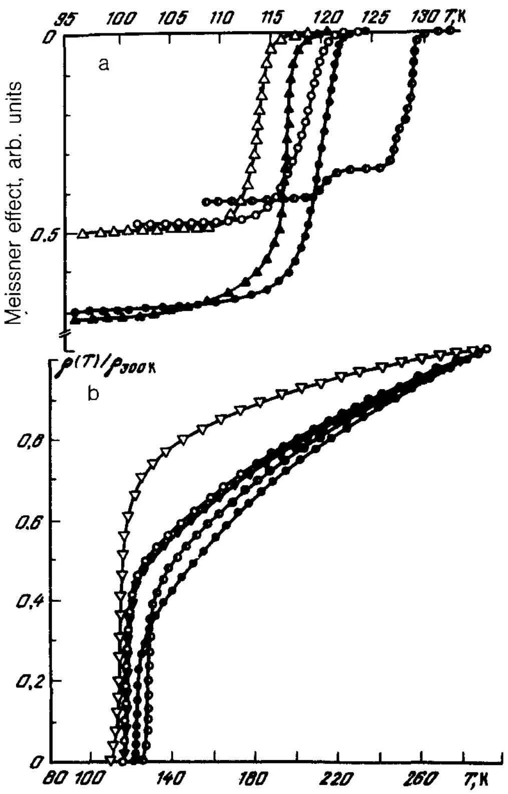

FIG. 3. Temperature dependence of the Meissner signal (a) and of the resistivity (b) of the $Tl_{1.4}BaCaCu_{1.5}O_y$ samples obtained by the two-stage method. ◑—Sample 6; ●—sample 7; ○—sample 8; ▲—sample 9; △—sample 10.

The results of the magnetic and resistive measurements, obtained on the basis of a two-stage technology of the samples, are shown in Fig. 3, a and b. Three samples, Nos. 8–10, had the same history (810 °C, 10 h), but their final synthesis occurred at different values of T_s (870 °C for 20 min, 860 °C for 5 h, 850 °C for 5 h, and 840 °C for 5 h). The nucleation of the superconducting phase which begins at 118.5 K (sample 10), 120.5 K (sample 9), and 123.5 K (sample 8) correlates with the increase of T_s. Sample 9 has a larger volume of the superconducting phase which is commensurable with V_{ph} of sample 7, whose history is different (850 °C, 10 h), although its second synthesis occurred at the same value of T_s, $T_s = 850$ °C. Superconductivity in sample 7 was detected at 124 K. In sample 6 the superconducting transition begins at 133 K, but the volume V_{ph} of the phase is much smaller than that of the other samples. As can be seen from Fig. 3a, there are two more superconducting phases (at 121 K and 127.5 K), but the phase at 130 K has the largest volume in comparison with the other two phases.

The values of ρ300 K for the two-stage samples are slightly lower than those for the single-stage samples: 4–0.9 mΩ·cm. The temperature dependence of the resistivity is also not rigorously linear at high temperatures, as in the case of single-stage samples. The T_c^0 of all the test samples is higher than 110 K: 110.2 K (sample 10), 115.5 K (sample 9), 115 K (sample 8), 120 K (sample 7), and 125.3 K (sample 6). We note that the highest critical superconducting transition temperature (sample 6) does not correspond to the largest volume of the superconducting phase.

A comparison of the results of experimental study of $Tl_{1.4}BaCaCu_{1.5}O_y$ samples synthesized under different conditions thus shows that a two-stage technology yields much higher values of the critical temperature, but the volume of the superconducting phase in this case is smaller than that of the samples fabricated on the basis of the single-stage technology.

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