Forming High-Temperature Superconducting Layers at the Interfaces between Nonsuperconducting Phases

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Abstract—An alternative technique for synthesizing high-temperature superconductor samples is proposed, in which superconducting layers should form on the surface of hard-melting Ho_2BaCuO_5 green phase grains immersed in the liquid phase $BaCuO_2 + CuO$.

High-temperature superconductor (HTS) structures of the 1-2-3 type are usually synthesized using conventional ceramic technology [1–3]. A desired HTS phase is formed by repeated grinding and annealing. As was noted in [4–6], during the HTS synthesis, a side nonsuperconducting phase called green phase with the chemical formula Re_2BaCuO_5 (Re = Y, Sm, Eu, Gd, Dy, Ho, Er, Tm, or Yb) can easily be formed [5, 7–9]. The available melt growth (MG) technique [10, 11] ensures better sintering of grains in bulk superconductors, which leads to an increase in the critical current density as compared with a value for HTSs obtained by conventional methods. In the MG process [10, 11], an HTS is heated above 1000°C (the peritectic temperature of the compound), where the HTS phase decomposes into the solid Re_2BaCuO_5 phase and the liquid phase with the $BaCuO_2 + CuO$ composition. Then, the system is cooled and the Re_2BaCuO_5 solid phase undergoes a peritectic reaction with the liquid phases for the repeated formation of an HTS compound [10, 11].

This Letter proposes a technique for obtaining unbound superconducting grains in a polycrystal on the basis of the MG method [10, 11]; in this technique, the $BaCuO_2 + CuO$ compound should be added to the Re_2BaCuO_5 (Re = Y or Ho) compound. The high-quality Y_2BaCuO_5, Ho_2BaCuO_5, and $BaCuO_2$ nonsuperconductors are prepared separately and, then, the HTS phase is obtained by solid-state synthesis. The synthesis is performed at a temperature of 880°C, which is much lower than the temperatures used in [10, 11]. At this temperature, the initial compounds are not decomposed and the HTS phase starts forming on the surface of grains of the Y_2BaCuO_5 compound or the harder-melting Ho_2BaCuO_5 green phase immersed in the $BaCuO_2 + CuO$ liquid phase. Using the asymmetric molar ratio of the Ho_2BaCuO_5 green phase and the $BaCuO_2 + CuO$ compound (e.g., 15 : 75 mol %), we deliberately deviate from the stoichiometry of an HTS with the 1-2-3 type structure and obtain Ho_2BaCuO_5 grains in the bulk of a polycrystal with the $HoBa_2Cu_3O_7$ HTS layer formed on their surface. This technique for obtaining HTS layers in the bulk of a polycrystal can be used to form superconducting layers of different configurations on the surface of the polycrystalline Ho_2BaCuO_5 compound, which is promising, for example, for producing high-Q microwave bandpass filters required by modern radio electronics. This study will be described in detail elsewhere.

Single-phase Y_2BaCuO_5, Ho_2BaCuO_5, and $BaCuO_2$ nonsuperconducting compounds were prepared from high-purity Ho_2O_3, $BaCO_3$, and CuO oxides in air by the solid-state synthesis using a conventional ceramic technology. The maximum synthesis temperature was 850°C for $BaCuO_2$ and ~1200°C for the Y_2BaCuO_5 and Ho_2BaCuO_5 compounds. X-ray diffraction analysis was carried out on a Bruker D8Advance powder diffractometer (Bruker AXS). The obtained X-ray diffraction patterns of the Y_2BaCuO_5, Ho_2BaCuO_5, and $BaCuO_2$ compounds are consistent with the crystallographic database (pdf@81-800 and pdf@38-1402); it can be unambiguously concluded that the synthesized compounds correspond in structure to the desired ones and contain no side phases.
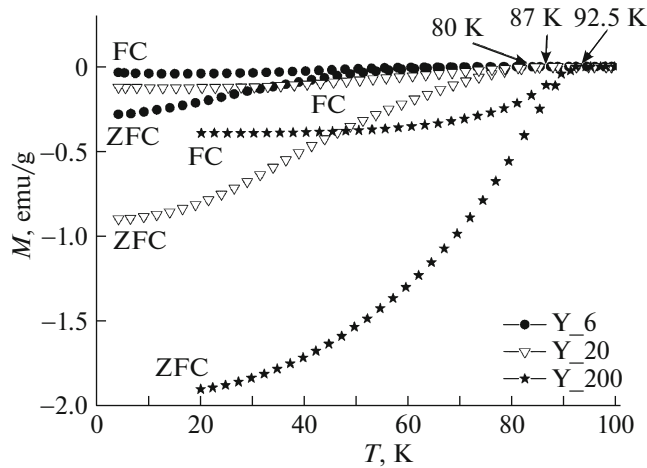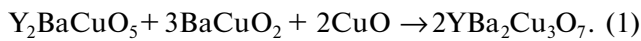
Fig. 1. Temperature dependences of magnetization for samples Y_6, Y_20, and Y_200 measured in the ZFC mode and the FC mode in a field of $H = 50$ Oe.

Fig. 2. Field dependences of magnetization for samples Y_6, Y_20, and Y_200 at a temperature of $T = 4.2$ K. Inset: comparison of the $M(H)$ dependence for sample Y_200 with the $M(H)$ dependence for the polycrystalline yttrium HTS from [13].

The Y_2BaCuO_5, $BaCuO_2$, and CuO compounds were used in the sample synthesis to obtain the desired HTS phase with the $YBa_2Cu_3O_7$ (1-2-3) structure. For this purpose, the samples were synthesized from the obtained compounds at a temperature of 880°C and different sintering times (6, 20, and 200 min). The HTS was obtained according to the scheme

$$Y_2BaCuO_5 + 3BaCuO_2 + 2CuO \rightarrow 2YBa_2Cu_3O_7. \quad (1)$$

In addition, scheme (1) was used to synthesize a sample based on the green phase with Ho containing 15 mol % of Ho_2BaCuO_5.

In this Letter, we used the following designations: Y_x are the samples of the expected $YBa_2Cu_3O_7$ composition synthesized according to scheme (1), where $x = 6, 20, 200$ is the time of sample annealing (min) at a temperature of 880°C and Ho_0.15 is the sample synthesized according to scheme (1), but containing only 15 mol % of Ho_2BaCuO_5. The differential thermal analysis of the $BaCuO_2 + CuO$ compound showed that its melting point is $T_m = 811.43$°C, which is significantly lower than the value for the Re_2BaCuO_5 (~1200°C) compound [6, 8]. During the synthesis at $T = 880$°C, the hard-melting green phase grains will be immersed in the $BaCuO_2 + CuO$ liquid phase. THTS synthesis should then occur at the green phase grain boundaries. In [12], the formation of the $YBa_2Cu_3O_{7-\delta}$ superconducting layer was observed in the reaction zone at the $BaCuO_2/Y_2BaCuO_5$ diffusion pair interface.

The temperature dependences of the magnetization for the synthesized samples were obtained in the zero-field cooling (ZFC) mode and in the field-cooling (FC) mode in a magnetic field of $H = 50$ Oe; the $M(H)$ dependences were measured at a tempe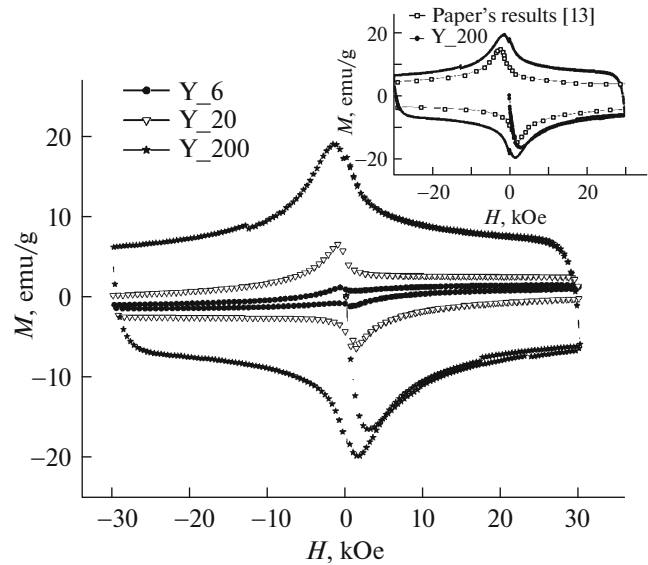rature of 4.2 K on a vibrating sample magnetometer of a quantum design physical property measurement system (PPMS) in magnetic fields from −90 to 90 kOe.

The temperature dependences of the magnetization for samples Y_6, Y_20, and Y_200 reveal a diamagnetic response in both the ZFC and FC mode. The superconducting transition temperatures are $T = 80, 87$, and 92.5 K for samples Y_6, Y_20, and Y_200, respectively (Fig. 1). In addition, a diamagnetic response was observed in the $M(H)$ hysteresis loops of these samples (Fig. 2). It is well-known from the literature that the diamagnetic responses of the $YBa_2Cu_3O_7$ HTS can attain 15−20 emu/g at $T = 4.2$ K [13]. For comparison, the inset in Fig. 2 shows the $M(H)$ dependences for sample Y_200 and the bulk polycrystalline $YBa_2Cu_3O_7$ HTS from [13]. Thus, the proposed technique for obtaining the HTS layers in the bulk of a polycrystal made it possible to obtain the $YBa_2Cu_3O_7$ HTS comparable in properties with the best polycrystals of this composition, where the HTS layers start forming at the boundaries of the hard-melting Y_2BaCuO_5 grains.

Figure 3 shows the $M(T)$ dependences for samples Ho_0.15 (right-hand scale) and Y_200 (left-hand scale); the inset in the figure shows the $M(H)$ dependence for sample Ho_0.15. It can be seen from the $M(T)$ dependence that superconducting transition temperature T_c for sample Ho_0.15 coincides with the T_c value for sample Y_200, while the diamagnetic response of sample Ho_0.15 is lower by approximately an order of magnitude. It can be seen from the $M(H)$ dependence that the diamagnetic response vanishes in a magnetic field of ~400 Oe. A value of 15 mol % of
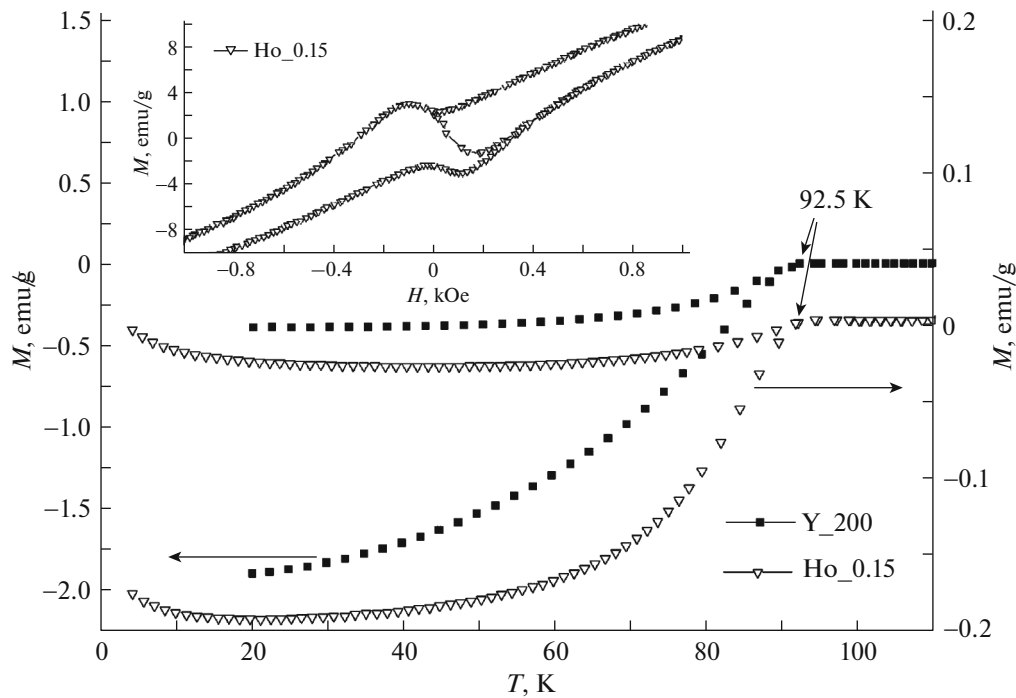
Fig. 3. Temperature dependences of magnetization for sample Ho_0.15 (right-hand axis) and Y_200 (left-hand axis) measured in the ZFC mode and the FC mode in a field of $H = 50$ Oe.

the Ho_2BaCuO_5 composition in the bulk of the sample is lower than the percolation threshold and we can say that there are individual noninteracting grains in a polycrystalline nonsuperconducting matrix, on the surface of which the HTS layers are synthesized. An increase in the volume of the superconducting phase of nonsuperconducting components was observed in the $La_2CuO_4 + La_{1.56}Sr_{0.44}CuO_4$ composites [14]. In [14], we managed to estimate the thickness of the superconducting layer, which was found to be several tens of nanometers.

It can be concluded on the basis of the above results of the magnetic measurements that superconducting transition temperature T_c increases with annealing time from 80 to 87 K for samples Y_6 and Y_20 and up to 92.5 K for sample Y_200 at an annealing time of 200 min. The results of the magnetic measurements of sample Y_200 confirm the formation of the 1-2-3 HTS structure with the diamagnetic properties comparable to those of the best polycrystalline HTSs obtained using conventional ceramic technology.

The T_c value for sample Ho_0.15 is 92.5 K, which indicates the formation of the 1-2-3 HTS phase; however, the diamagnetic signal at helium temperatures is lower than for sample Y_200 by an order of magnitude. Since the melting point of the Y_2BaCuO_5 and Ho_2BaCuO_5 compounds is higher than 1200°C [6], which exceeds by far the melting point of the $BaCuO_2 + CuO$ compound, the superconducting layers in the investigated samples should start forming on the sur-

face of the hard-melting Ho_2BaCuO_5 or Y_2BaCuO_5 grains immersed in the $BaCuO_2 + CuO$ liquid phase.

Due to the asymmetric molar ratio of the initial components in sample Ho_0.15, the HTS phase starts forming as layers on the surface of the Ho_2BaCuO_5 hard-melting phase grains and represents a set of noninteracting HTS grains in a nonsuperconducting polycrystalline matrix.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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